

Synthesis of Intermetallics and Nanocomposites by High-Energy Milling

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Abstract Elemental powders are used in high energy milling processes for the synthesis of new compounds. The low temperature solid state reactions during milling in inert gas atmosphere may result in intermetallic phases, carbides, nitrides or silicides with a nanocrystalline structure. To obtain dense materials from the powders a pressure assisted densification is necessary. On the other side the defect-rich microstructure can be used for activated sintering of elemental powder mixtures to obtain dense bodies by pressureless sintering. Results are discussed for nanocrystalline cermet systems and for the sintering of aluminides and silicides.

Keywords: nanocomposites, intermetallics, high-energy milling, elemental powder mixtures, pressureless sintering, activated sintering

1. Introduction

The processing of nanostructured materials has become an important field in materials research during the last two decades. The preparation of such materials has been realised by different methods, e.g. by compaction of nanopowders prepared by evaporation-condensation method or by CVD processes or using sol-gel processes. Other methods use PVD-techniques or severe plastic deformation to transform the material in the state far from equilibrium. An interesting method to obtain nanocrystalline structures comes from the mechanical alloying technique.¹⁻⁶⁾ High energy milling of powder mixtures can be used to obtain grain sizes in the nanometer range of the phases formed during milling. The powder particle size in this procedure is in the range of micrometers thus enabling a processing of the powders at normal atmospheres. Furthermore the high energy milling process can be used to prepare heterogeneous powder mixtures with very fine phase distributions that show high activity during sintering. The processing of materials strengthened by dispersions with nanometer size obtained by high energy milling will be reported elsewhere.⁷⁾

In this paper the formation of nanocrystalline hard compounds from the refractory metals Ti, V, Zr and Nb and a metalloid C, N, B by high energy ball milling is

discussed. The studies included the formation of nanocrystalline hard phases and composites with a metal matrix, i.e. Ni, Fe and Co. The mechanism of formation was investigated for the variation of milling intensity and time by X-ray diffraction of phases and by in-situ thermal analysis measurements during milling.⁸⁾ The same method was applied to study the processes in silicide and aluminide systems during milling. These powders were also studied for their sintering behaviour.

2. Experimental Procedure

For all investigations elemental powders with normal particle sizes between 10 and 150 μm were milled in a planetary ball mill. The milling vials and balls (diameter 10 mm) were made out of hardened steel and the powder to ball ratio for most experiments was 1:10, in some experiments also 1:20 or 1:5. The milling intensity was adjusted by varying the speed of revolution and milling times of up to 48 h were used. All powder handling was done in an argon atmosphere to prevent reactions with gases. However the experience shows, that most powders also can be handled on air. The powders were examined by metallography, x-ray diffraction, SEM and TEM, the milling process was studied using the GTM-system (Gaspressure-Temperature-Measurement).⁸⁾ Sintering was investigated in a

Netzsch dilatometer. In addition the specific surface of the powders was measured and DSC (differential scanning calorimetry) measurements were performed. The consolidation of the powder was done by hot isostatic pressing or by pressureless sintering in a dilatometer.

3. Nanocrystalline Hard Materials and Nanocomposites

In all binary systems investigated a typical lamellar microstructure was observed in the first stage of milling. The reaction between the refractory metal and the metalloid occurred rapidly if enough energy was supplied from the milling process. After reaction x-ray diffraction pattern shows only the peaks of the hard phase. In Fig. 1 this is demonstrated for the Zr-C system after different milling times. The energy (varied by milling time or speed) required for the activation of hard phase formation depends on the heat of formation of the relevant phase (Fig. 2). DSC measurements with

milled powders in the state before the reaction show a broad exothermic effect in the range between 100 and 900°C with a sharp exothermic peak superposed in the range 500-800°C. This peak is not observed after phase formation during milling (Fig. 3). If an element of the iron group is additionally introduced to the system the formation of the hard phase is similar to the reactions in the binary mixture. The metal added (Fe, Co, Ni) does not take part in the reaction. Fig. 4 shows the x-ray diffraction pattern for the Ti-C-Ni system for different milling times. It is interesting to mention that up to 25 wt-% metal additions no x-ray detection of the metal phase was possible. It may be concluded that metal atoms are in solution in the grain boundaries of the hard phase having a grain size of several nanometer.

In the as-formed state the hard material phases

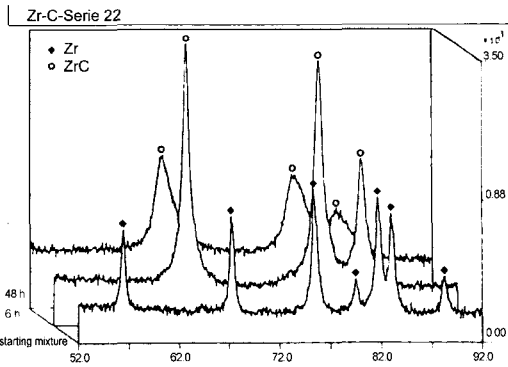


Fig. 1. X-ray diffraction pattern (Co-K radiation) of Zr + C system after different milling times.

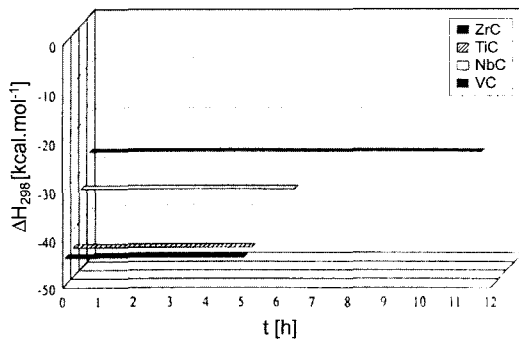


Fig. 2. Milling time required for carbide formation is found for different heats of formation of the carbides.

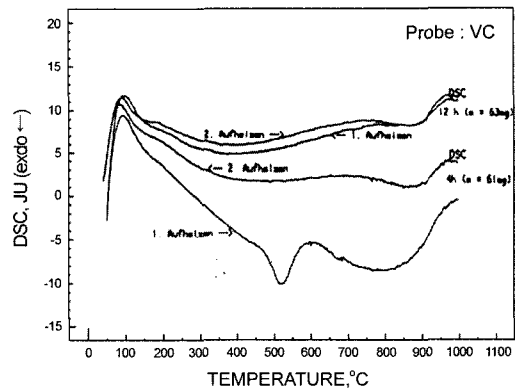


Fig. 3. DSC measurement for V-C samples after high energy milling. No carbide was formed during milling.

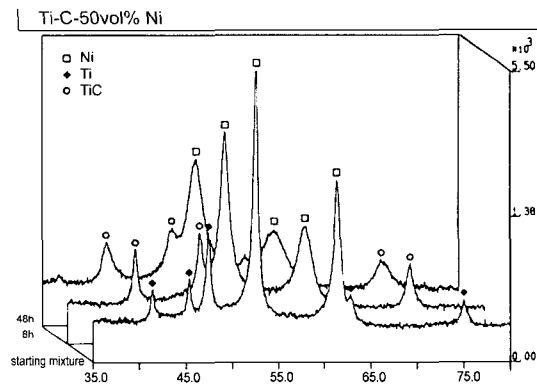


Fig. 4. X-ray diffraction pattern (Co-K radiation) of the Ti + C + Ni system after different milling times (50 Vol-% Ni).

show a crystallite size of 40-100 nm determined by x-ray method. Continued milling results in a decrease in crystallite size to 7-8 nm after milling times of 16-20 h for all systems investigated (all phases show fcc structure). Further milling up to 48 h did not change the crystallite size (Fig. 5). In contrast to these results the strains determined from the x-ray measurements continuously increased with milling times up to 48 h and reaches a very high value of nearly 1% (Fig. 6). In ternary systems (with binder metal content >25%) both the hard phase and the metal phase have a nanocrystalline structure as was observed by TEM.

The average particle size of the powder during milling was reduced to values of about 0.1-1 μm that is two orders of magnitude larger than the crystallite grain size. The SEM investigations of the powders showed a wide range for the particle size distribution. The particle size reaches a constant value after longer

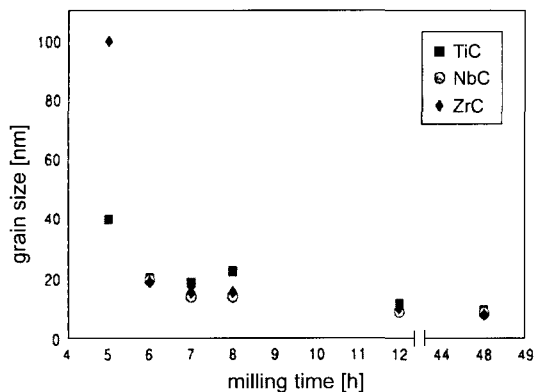


Fig. 5. Grain size of carbides formed during milling after different milling times (determined from X-ray results).

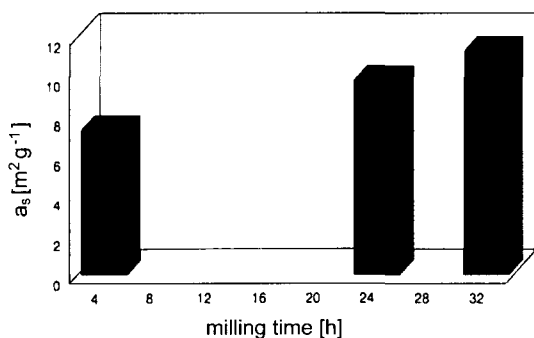


Fig. 6. Accumulated strain in the carbide phase after different milling times (determined from X-ray results).

milling as was seen from the specific surface area measurements (Fig. 7). Nanocomposite powders with metal additions resulted in bigger particle sizes that led to specific surface areas of only 0.5 to 2 m^2/g .

To study the processes directly in the milling system a measuring unit was developed that allows the determination of the gas pressure and the temperature in the closed milling vial.⁸⁾ Especially the gas pressure that is proportional to the gas temperature showed to be very sensitive for rapid exothermal reactions. The results of in-situ measurements are shown in Fig. 8. By the heat released due to friction the temperature is slightly increased with milling time. After a critical time, which depends on the milling intensity and the heat of formation of the hard phase, a rapid temperature peak indicates the phase formation. Due to the high heat capacity of the milling system after this the

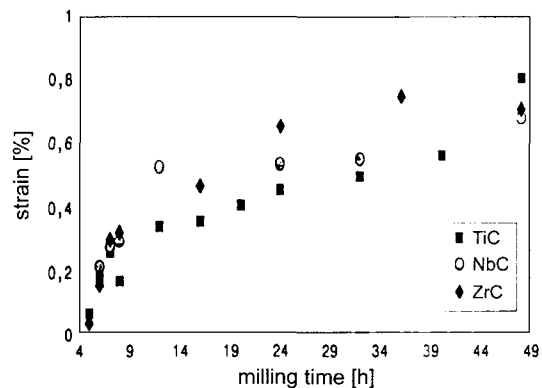


Fig. 7. Specific surface of TiC powder formed by high energy milling after different milling times.

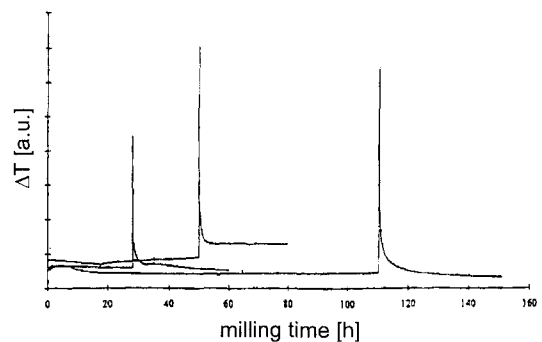


Fig. 8. In-situ temperature measurements during milling of Ti-C powder mixtures for different ball-to-powder ratio. a) 20:1, b) 10:1, c) 5:1.

gas temperature decreases within a short time. Powders analysed after the peak occurred showed a complete reaction of all the material.

From the results the process of phase formation and the factors influencing the process can be discussed as follows. During milling the collision of the balls transfers the kinetic energy to the powder particles between them. The heavy deformation increases the temperature inside the powder particles. The temperature that may be reached is estimated by 450-650°C. Due to the cooling effect of the balls in close contact with the powder this temperature is present only for milliseconds. If the refractory metal phase and the metalloid are in contact during this period, some diffusion is possible to form the hard phase. This is connected with a release of energy due to the heat of formation of the new compound. The amount of energy Δq in the single diffusion zone gives a rise of the powder temperature $\Delta t = \Delta q/c_p$ (with c_p the heat capacity of one powder particle). With increased milling time the formation of lamellar structures and nanodispersed states of the two phase lead to multiple diffusion zones inside one powder particle. The temperature increase from the heat of phase formation is then $\Delta T = N \Delta q/c_p$ (where N is the number of diffusion zones in the particle). This temperature increase has to be added to the starting temperature of 450-650°C. The increased temperature accelerates the diffusion and more heat is generated. Additionally the diffusion is enhanced by the high concentration of lattice defects introduced by

milling. In the first stage the cooling effect from milling balls is high enough to cool down the system and to stop the diffusion. If a critical number of diffusion contacts is reached, the heat generation is faster than the heat transfer to the balls. The powder particles heat up to very high temperatures by a self activating reaction (maximum temperatures may reach 4500°K).

The statistics of powder microstructures should lead to a process that takes some time for the reaction of all powder particles. The general increase of temperature if owe to the reaction brings also powder particles not being reached the critical microstructure to a higher temperature and they can react too. This model explains also why milling intensity is important for the reaction. Low intensity gives lower temperature differences during collisions of the balls as the starting temperature for diffusion. On the other side long milling at low intensity will lead to broader diffusion zones between the phases. The less steep concentration gradient gives less heat release during an individual impact and a finer dispersion is necessary to reach the critical state. At very low intensities of milling the spontaneous phase formation was not observed even for very long milling times. Table 1 gives an overview of all systems studied and the phases found after reaction.

4. Synthesis of Silicides and Aluminides

The high energy milling process was also applied to manufacture intermetallic phases by using elemental

Table 1. High energy milled systems and phases found after prolonged milling

Starting mixture	Milling product
Ti + C + < 15 vol% Fe or Ni + 50 vol% Fe or Ni	TiC TiC, Fe or Ni could not be detected by X-ray analysis TiC in a Ni/Fe matrix, both phases nanocrystalline (Ni/Fe partially amorphous)
Ti + B + < 10 vol% Fe or Ni + 50 vol% Fe	TiB ₂ TiB ₂ , Fe or Ni could not be detected FeB + TiFe
Ti + C + B + < 10 vol% Fe	TiC + TiB ₂ TiC + TiB ₂ , Fe could not be detected
Ti + Si	Ti ₅ Si ₃
Zr + C, Nb + C	ZrC, NbC
Zr + B, Nb + B	ZrB ₂ , NbB ₂
V + C	VC
Mo + Si	MoSi ₂
Si + C	SiC
Fe + C	Fe ₃ C + Fe, both phases nanocrystalline

powder mixture. Some aluminides and silicides in recent years were discussed as potential candidates for high temperature applications. An economic way for the production of net shape parts could start from low cost elemental powder mixtures and combine the phase formation and sintering during heat treatment. As was shown earlier,⁹⁾ sintering of mixed powders in most cases is connected with swelling effects of the compacts resulting in decreased densities.

As demonstrated for hard phases the high energy milling process can be used to adjust a very fine distribution (down to nanometer) of the starting elemental materials in the powder particles formed during milling. Studies of the sintering behaviour of previously activated powder mixtures were performed for the systems Mo-Si, Ti-Si, Ti-Al, Ni-Al and Fe-Al.⁹⁻¹⁷⁾ For all systems a principle change in the sintering behaviour can be observed after milling (Fig. 8). If the crystallite size was decreased to submicron dimensions, the phase formation occurs in the solid state. As was shown by detailed studies for the system Ti-Al,⁹⁾ this prevents most of the swelling effects. The solid state reaction sintering however is still connected with mechanisms leading to a density decrease. At the individual contacts between the elemental powder phases the interdiffusion produces pores. However their size is in the same range as the crystallites size and the small radius of curvature produces a highly increased driving force for sintering and causes an immediate annealing parallel to pore formation. The dilatometric curve therefore shows only shrinkage for all temperatures. The reaction of the elemental components is connected with an increase of the density of the system. As could be demonstrated for Mo-Si system, a milling process

with partially formed MoSi_2 phases during milling gives the highest densities after sintering.¹⁶⁾ Further milling results in complete reaction of the powder by the mechanism discussed for nanocrystalline hard materials. To reach the optimum with a partial phase formation the milling process has to be performed with a lower intensity to prevent a complete spontaneous reaction of the powder.

The concept described for binary systems can be applied also for the manufacture of composites. The additional phase can be introduced as a fine powder distributed evenly during milling or may be formed by solid state reactions too. In detail composites with a matrix of MoSi_2 and SiC or ZrO_2 as a second phase were studied.¹⁷⁾ The fracture toughness of the material could be increased from $4.1 \text{ MPa} \cdot \text{m}^{1/2}$ for the single phase silicide to $10.8 \text{ MPa} \cdot \text{m}^{1/2}$ for the composite system with 15 wt-% ZrO_2 .

5. Conclusions

The high energy milling of elemental powders is a relatively simple way to produce hard phases and intermetallics from cost effective raw materials. The dispersion of phases down to nanometer dimensions and the high concentration of lattice defects in the powders is the reason that solid state reactions between the components occur at very low temperatures. For many systems the direct synthesis during milling is possible and leads to nanocrystalline microstructures in the powders. The powder particles themselves have sizes in the micrometer range and can be processed at normal atmospheric conditions. For the reaction sintering of elemental powder mixtures the high energy milling opens up a possibility for pressureless sintering without swelling effects. This gives high densities with closed porosity of the final product. Powder metallurgy forming techniques like uniaxial compaction or MIM can be applied for part production using inexpensive starting powders.

References

1. Y. Ogino et. al : Materials Science Forum, Vol. 88-90 (1992) 795.
2. G. Le Caer et al.: J. Mater. Sci., **25** (1990) 4726.
3. P. Matteazzi et. Al: J. Hard Materials, **2** (1991) 171.
4. A. A. Popovich et al.: Materials Science Forum, Vol. 88-90 (1992) 737.

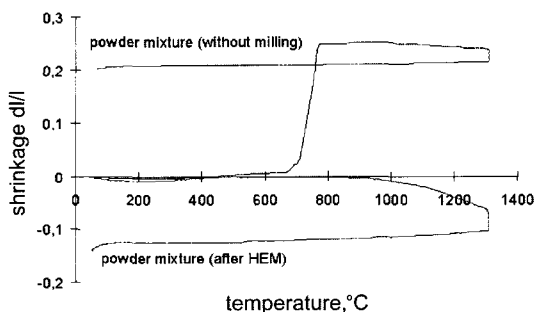


Fig. 9. Shrinkage curves of compacts during reaction sintering of Ti-Al powder mixtures prepared without and with high energy milling of the starting elemental powders.

5. M. S. El-Eskandarany et. al: Materials Science Forum, Vol. 88-90 (1992) 801.
6. P. Matteazzi et al.: Proc. Powder Metall. Word Congress PM94, Paris, Vol. III, 1815 (1994).
7. T. Weissgaerber et al.: Proc. 1st Korea-German Symposium on Nanomaterials, 18-19. Nov. 2002, Ulsan, Korea, in print.
8. R. Scholl, R. Wegerle, W. Mutter: Journal of metastable and nanocrystalline materials, Vol. 8 (2000) 964-972.
9. A. Böhm: "Untersuchungen zum Reaktionssintern von Ti-Al-Pulvermischungen", Verlag Mainz, Wissenschaftsverlag, Aachen (2001).
10. R. Scholl, A. Böhm, B. Kieback: Materials Science and Engineering **A261** (1999) 204 -211io.
11. T. Schubert et. al.: Intermetallics, 10 (2002) 873 -878.
12. R. Scholl, T. Jüngling, B. Kieback: Werkstoffwoche 96, Werkstoffe f. d. Energietechn., Symp. 3, Stuttgart, Band **3** (1997) 213-218.
13. A. Böhm, B. Kieback: Z. Metallkd. **89(2)** (1998) 90- 95.
14. R. Rein: Thesis, Universität Stuttgart (1996).
15. M. Franke: Diploma-Thesis, Technische Universität Dresden (2001).
16. T. Schubert et. al.: Mat.-wiss. u. Werkstofftech. **33** (2002) 1- 4.
17. M. Zumdick, A. Böhm, R. Scholl, T. Schubert, B. Kieback: MATERIALS WEEK 2000 and 2001 Proceedings, CD 2, Ed. Werkstoffwoche-Partnerschaft GbR, Publisher: Werkstoff-Informationsgemeinschaft mbH, Frankfurt, 2002.