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Synthesis and properties of nanocrystalline compounds prepared by high-energy milling

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Abstract

Carbides, borides and nitrides of high melting transition metals were synthesized by high energy ball milling of elemental powder mixtures. The obtained hard material phases show a nanocrystalline structure with a saturation value of the crystal sizes between 7-8 nm. The kinetics of the reaction were investigated, and the nanocrystalline powders were densified by HIP.

Introduction

The formation of nanostructure materials has become a wide field in material research in recent years. The preparation of these materials has been realized by different methods, for instance by evaporation in an inert gas atmosphere and condensation or by a sol - gel process.

In this paper we report the formation of nanocrystalline hard material phases from a high melting transition metal, i. e. Ti, V, Zr, or Nb and a metalloid, i. e. B, C, or N, by high energy ball milling. Hard material phases were prepared single - phased or in ternary systems with a metallic component, i. e. Ni, Fe, or Co. The formation mechanism of nanocrystalline phases and compounds was investigated by a variation of the milling intensity and time. The influence of different heats of fusion was also analysed.

Bulk material were prepared by means of pressure aided consolidation techniques. In further research the properties of the consolidated nanostructured samples will be investigated .

Experimental Procedure

Mixtures of elemental powders having particle sizes between 10 and 150 μm were milled in a planetary ball mill. The milling vials and balls (10 mm diameter) were made of hardened steel, and the powder - to - ball ratio was about 1 : 10. The milling intensity was adjusted by varying the speed of revolution, and the milling time up to 48h. All powder handling was done in an argon atmosphere.

The powders were examined by metallography, x - ray diffraction and SEM and TEM. The specific surface area was determined, and differential scanning calorimetry experiments were carried out.

The consolidation of the nanocrystalline powders was done by hot isostatic pressure, or by model sintering in a dilatometer.

Results and discussion

Phase Formation

In all binary systems investigated in this study the typical lamellar microstructure was observed in the first stage of milling. The reaction between metal and metalloid occurred rapid and complete if enough energy was supplied. X-ray diffraction pattern shows the peaks of the hard material phase only. In fig. 1 this is demonstrated by the Zr - C -system for different milling times. The energy, i. e. the milling time, required for activation of hard material phase formation varies with the heat of fusion of the relevant phase (fig. 2). DSC curves of milled powder mixtures in the state before reaction show a broad exothermic effect in the range between 100 and about 900 °C and a sharp peak by 500- 800°C .This peak is not observed after phase formation,(see fig. 3).

If an element of the iron group of PSI is present the formation of hard material phases is analogous to the reaction in the binary mixture, the metallic component(Fe, Ni, or Co) does not take part in the reaction. Fig. 4 shows the x - ray diffraction pattern of Ti - C - Ni for different milling times. Up to 25 wt% metal in the powder mixture , the metallic component was completely dissolved in the grain boundaries of the hard material phase.

Crystal Size and Powder Dispersity

In the as formed state hard material phases show a x - ray determined crystallite size between 40 - 100 nm . Continued milling results in a decrease in crystallite size to a saturation value of (7-8) nm after a milling time of about 16 - 20 h for all investigated phases with fcc structure. Milling up to 48 h does not reduce the crystal size, see fig. 5 .

In contrast to this the x - ray determined strains increase continuously until 48 h milling time and reach maximum values of nearly 1% (fig. 6).In ternary systems both hard material phase and metallic phase show a nanocrystalline structure wich can be observed in TEM .

The average grain size of hard material powder particles is been reduced during the milling procedure to values between 0,1 - 1 micrometers, i.e. about two orders of magnitude larger than crystal size.SEM - investigations ofpowders after milling show a wide particle size distribution. The particle size exhibits a saturation too. This can be observed by measuring of the specific surface area, shown in fig. 7 . Two - phase powders have remarkably higher particle sizes,demonstrated by specific surface areas of about 0,5 - 2 m²g⁻¹.

Consolidation

Sintering behaviour of nanocrystalline powders was investigated by dilatometry. Fig.8 shows the results of TiC in different milling states in comparison to conventional crystalline sample. Nanostructure materials start to shrinke at a temperature of about 1000°C. TiC with an average grain size of 1 µm exhibits no shrinkage up to 1500°C. In two - phase nanocrystalline samples the start of shrinkage occurs at distinct lower temperatures than in conventinal cermet with the same composition.

Consolidation by hot isostatic pressing was done at temperature of 950°C and a pressure of 100MPa. The consolidated samples exhibit residual porosity and an inhomogenous microstructure.

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

Fig. 3: DSC scan for V-C after 4h milling processing

Fig. 2: Milling time required until the carbide formation for variant heat of fusion

Fig. 4: X-ray diffraction pattern (Co-K radiation) of Ti + C + Ni after different milling times

Fig.6: X - ray determined strain as function of the milling time

Fig.5: X - ray determined grain size as function of the milling time

Fig.8: Shrinkage of nanocrystalline ball milled TiC powder

Fig.7: Specific surface area of TiC after milling

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