Ceramics International 23 (1997) 39–44

0272-8842/97 $17.00+.00
0272-8842(95)00138-7

Synthesis of Nanostructured Materials by Mechanical Alloying

Paolo Matteazzi,[a] Gerard Le Caër[b] & Alain Mocellin[b]

[a]Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, Via Cotonificio 108, I-33100, Udine, Italy
[b]Laboratoire de Science et Gènie des Matèriaux Mètalliques associè au CNRS U.R.A. 159, Ecole des Mines, F-54042, Nancy Cedex, France

(Received 3 August 1995; accepted 28 September 1995)

Abstract: Materials can be processed by grinding not only for comminution, but also to obtain a variety of structures (amorphous, nanophased), fine mixing of phases, alloys and to directly synthesize compounds such as carbides. Nanocomposites can also be synthesized by reduction, exchange and mixing reactions driven by grinding, as well as by combining the above processes. Large scale economical production of such materials is feasible by grinding in mills designed for that purpose. The mechanical properties of materials are enhanced by the nanophase structure. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Grinding is no longer used for the sole purpose of reducing the sizes of particles of all kinds of materials. Grinding is also a method of synthesis of advanced materials, called mechanical alloying,[1] which has received considerable attention in recent years.[2] Mechanical alloying (MA) is basically a dry, high-energy milling process, which was originally developed as a means to manufacture oxide dispersion-strengthened superalloys for jet engine parts. The feasibility of synthesis of a large variety of materials, from metallic to ionic (alloys, compounds, composites) with a diversity of structures (quasi-crystalline, crystalline, amorphous) by milling of elemental mixtures in a ball mill is now well established (mechanosynthesis).

Moreover, grinding is a way of disordering solids and of inducing or activating phase transformations or chemical reactions (mechanochemistry).[3,4] MA also appears to be an attractive method of synthesis (mechanosynthesis) in view of its potential for large scale production. The synthesized materials, often with non-equilibrium structures, include among others, crystalline materials with nanometre-sized grains.

MA will be of great interest if the synthesized powders can be consolidated with a limited grain growth and without porosity, giving rise to materials with improved mechanical properties. For instance, superplasticity is expected to be significantly enhanced in large, fully dense nanocrystalline ceramic compacts.[5] More generally, all kinds of oxide or non-oxide ceramic materials, alloys strengthened by a dispersion of refractory oxide particles, and ceramic–metal composites, may be synthesized by MA of powder mixtures or by reactive milling.[6,7] The use of grinding for inducing phase transformations and even amorphization has been/is being thoroughly investigated, in particular in oxides.[8,9] The present paper describes the considerable potential of MA for synthesizing ceramic and ceramic–metal composite powders with nanometre-sized grains and some properties of materials consolidated from such powders.

2 SYNTHESIZED MATERIALS

2.1 Experimental conditions

Reaction milling experiments were mainly performed in high energy mills at laboratory scale, such as in the vibratory ball mill Spex® 8000 mixer/mill and in the planetary ball mill Fritsch® Pulverisette. Experiments reported in this paper were all performed in dry conditions, using grinding means and vial constituted of WC or steel. The ball to powder weight ratio (BPR) is varied in the range 5:1–40:1. The initial powder mixture (either elements and/or compounds) is introduced in the vial, usually under controlled atmosphere, and milled either using continuous milling or adopting rest periods to allow cooling of the vial. The temperature raise of the vial does not usually exceed 100 °C, and processing is assumed to be essentially at room temperature. In general, milling times required to complete the syntheses do not exceed 10–15 h. The powders were characterized by 57Fe Mössbauer spectroscopy (isomer shifts are referred to α-Fe) and X-ray diffraction (XRD) using CoKα ($\lambda = 0{\cdot}1789$ nm) radiation. The mean crystallite size was calculated from the broadening of the X-ray peaks corrected for instrumental broadening.

2.2 Synthesis of compounds from elemental powders: carbides and intermetallics

The direct synthesis of carbides was obtained by grinding a powder (or chips, or even pieces of some mm in size) mixture of a metal and graphite.[10,11] The formation of stable, metastable, mixed and new carbides having crystal sizes in the range 10–20 nm was observed (some of the syntheses were also performed in air), such as for SiC, TiC, WC, ZrC, VC, MoC, ReC, HfC_x ($x < 0{\cdot}82$), VC_x ($x < 0{\cdot}5$), $NbC_{0{\cdot}75}$, NbC_x ($x < 0{\cdot}5$), MoC_x ($x < 0{\cdot}5$), Cr_3C_2, Mn_3C, Fe_3C, Fe_7C_3, Fe–C alloy (martensite-like), Co_3C, Ni_3C, Al_4C_3, mixed-(TiAlV)C, $(TaRe)C_x$, $(FeW)_{3;6}C$. Mixed carbides were formed either by milling an alloy with graphite or a powder mixture of metals and graphite, or from a carbide and a metal.[10,12] Metal–carbon alloys can also be synthesized as shown in Refs 10 and 13 in the $Fe_{1-x}C_x$ system ($x < 0{\cdot}15$) in which an Fe–C alloy, martensite-like, was obtained.

The direct, room temperature synthesis of nanophased (crystal size in the range 9–15 nm) silicides,[11,14] mainly with composition MSi_2 (M = Fe, Co, Ni, Cr, Mn, Mo, Re, Hf, Ta, V, Zr, Nb, Ti, W), was similarly obtained by grinding "M" metals with Si. Single phases according to the respective phase diagrams are often obtained, but in some cases polyphased products were observed, such as in the $FeSi_2$ and $MoSi_2$ systems, where both low (β-$FeSi_2$, α-$MoSi_2$) and high (α-$FeSi_2$, β-$MoSi_2$) temperature phases were observed.[14] The following silicides have been obtained by mechanosynthesis: FeSi, (α, β)-$FeSi_2$, $HfSi_2$, $ReSi_2$, Re_5Si_3, (α, β)-$MoSi_2$, $ZrSi_2$, $TaSi_2$, Ta_5Si_3, VSi_2, Ni_3Si, Ni_3Si_2, MnSi, Mn_5Si_2, $TiSi_2$, CoSi, $CoSi_2$, $NbSi_2$, WSi_2, β-W_5Si_3 and γ-$CrSi_2$. Other intermetallic compounds obtained in this way include aluminides (Fe_3Al, $TiAl_3$, $TaAl_3$, NiAl), stannides ($FeSn_2$, FeSn), and germanides (FeGe, Fe_3Ge).

Exchange and mixing reactions driven in a high energy mill can give rise to the formation of nanocomposites.[12] Iron-containing compounds (nitride, cementite) were used in the following generic reaction schemes:

$$Fe_{2{\cdot}5}N + Al \rightarrow AlN + 2.5Fe \qquad (1)$$

$$4Fe_{2{\cdot}5}N + 3Si \rightarrow Si_3N_4 + 10Fe \qquad (2)$$

$$Fe_3C + Cr \rightarrow (Fe, Cr)_{Carbide} \qquad (3)$$

In the cases of reactions (1) and (2), the formation of Al and Si nitrides (crystallite sizes of 8 and 22 nm, respectively), together with iron aluminides or silicides, and iron alloys were obtained. Milling of Fe_3C with Cr [reaction (3)] led to a complete transformation of cementite to an amorphous $(Fe–Cr_{rich})C$ phase and a mixed (Fe,Cr)C carbide.

2.3 Synthesis of metal/oxide nanocomposites

Chemical reactions may be influenced by external mechanical actions.[3,15] A mechanical action may:[15] (1) involve a chemical reaction which serves as one channel for the dissipation of mechanical energy which is provided to the ground powders, or (2) lead to non-equilibrium states with enhanced reactivity which may be retained over a long period after removal of the action. Both ways may be used to synthesize materials in one-step or in multi-step processes. Metal–oxide composites are in general prepared either by direct grinding of mixtures of metallic and oxide powders, or by reactive milling involving redox reactions. The former composites mainly belong to the family of oxide-dispersion strengthened (ODS) alloys, while the latter mainly belong to the cermet family with a large oxide volume fraction. We will successively describe some general characteristics of ODS alloys and of cermets synthesized by mechanical alloying.

2.3.1 ODS alloys

MA has been extensively used for producing Fe-, Ni- and Al-based ODS alloys.[1,16] In general they contain a volume fraction of oxide particles of about 1–2 vol%. The ODS alloys have already found applications in various areas due to a unique combination of high temperature strength and environmental resistance.[16] Yttria is the most widely used oxide, but alumina or rare-earth oxides have also been recently dispersed in intermetallic compounds.[16] For instance, a fine and homogeneous dispersion of alumina (1 wt%) formed during attrition of a B2 FeAl aluminide improves the creep resistance at high temperature (≈700 °C).[17]

For the future, MA may be used to synthesize advanced alloys for aero-engines including intermetallic compounds and composites based on Ni, Ti, Al and Nb.[16]

2.3.2 Cermets

Much attention has been devoted to the aim of combining metals and ceramics in order to generate materials with improved properties. More recently, processes based on mechano-chemical reactions have been investigated[3–7,15,18–23] and attention has been paid to the understanding of the mechanisms and principles which govern such reaction syntheses. The synthesis of alumina-based cermet powders involves displacement reactions between aluminium and either one or a mixture of metal oxides. Such oxido-reactions induced by the grinding process can be schematically written as $(3/y)M_xO_y + 2Al \rightarrow Al_2O_3 + (3x/y)M$ when they are performed in stoichiometric proportions. The latter reactions yield, in general, composites mainly made of α-Al_2O_3 and M with nanometre-sized grains. The calculated volumetric fraction of alumina ranges between 48 and 72% according to the metal oxide.[7] Systems of particular interest are α-Al_2O_3–Fe,Cr,Ni. Alumina–iron composites have been prepared by the reduction of hematite[7,20–25] or of magnetite by aluminium.[25] In both cases, the composite synthesis takes place in three stages:[25] (i) incubation period; (ii) high temperature combustion during which a non-uniform mixture of final and intermediate phases, like hercynite $FeAl_2O_4$, forms;[7,20–23,25] and (iii) gradual disappearance of transient phases[7,20–23,25] and particle refinement of the reaction products by grinding. 57Fe Mössbauer spectra clearly reveal that α-Fe dissolves some at% of Al.[7,20–23] They also show low intensity central components observed after Fe implantation in alumina.[26] They are associated partly with Fe^{2+} in hercynite type environments and partly with either Fe^{3+}, Fe^{4+} or, more likely, with iron clusters in α-Al_2O_3.[26] The experimental results reported for the mechano-chemical reduction of hematite by aluminium in stoichiometric proportions are consistent with a model involving three separate reaction steps.[23] If the redox reaction of magnetite is performed with varying proportions of aluminium,[25] transition alumina γ-Al_2O_3 is observed to occur. Such transition aluminas are, however, transformed into α-Al_2O_3 by prolonged grinding. Alumina–iron nanocomposites may as well be prepared by direct grinding of a mixture of Al_2O_3 and of Fe powders.[22] Their Mössbauer spectra also show a central component, as for those composites synthesized by reactive milling, but with a slightly lower intensity. Moreover, iron does not dissolve aluminium as in the latter materials. It would be interesting to compare the properties of the cermets consolidated from those two types of powders. Composites of alumina with an alloy, for instance α-Al_2O_3–$(Fe_{1-x-y}Ni_xCr_y)$, are obtained by grinding a mixture of aluminium and iron, nickel and chromium oxide powders in the required proportions.

In many cases, a self-sustaining (combustion) reaction takes place during MA owing to a high negative enthalpy.[6] MA significantly increases kinetics in such displacement reactions by the dynamic maintenance of high reaction volumes and rapid diffusion rates related to short diffusion paths, enhanced defect density and high reaction interface areas.[6] In highly exothermic redox reactions, a mechanically induced combustion propagates through the unreacted powders after an incubation period, which is the time required for the process to reduce the critical ignition temperature to less than the local temperature reached by particles during a collision event.[6]

Exchange reactions of the type above ($MO + R \rightarrow M + RO$) have been used to produce a variety of metal–oxide nanocomposites by MA, such as for M = (Fe, V, Cr, Mn, Co, Ni, Cu, Zn, Nb, Mo, W, Si) and R = (Al, C, Ti, B, Cr, Si).[7,24] Some of the nanocermets obtained are listed below: α-Al_2O_3–(M listed above or alloys such as Fe,Ni,Cr); α-Al_2O_3–Ti; α-Al_2O_3–Sn; B_2O_3–Fe–Fe_2B; Cr_2O_3–$FeCr_{alloy}$; SiO_2–Fe; TiO_2–W; SiO_2–Nb.

3 EVALUATION OF PRODUCTION ASPECTS

The production of nanophase materials in large quantities and at low costs requires a mill having: (a) high impact velocities of the grinding balls; (b) high impact frequency for each ball; and (c) easy scale-up of the mill capacity. At least one of the above criteria is not satisfied in currently, commercially available mills. A high-capacity high-energy mill (HCM) was therefore developed,[27] and is shown in Figs 1 and 2: it basically consists of a vial, a system to compensate the inertial forces and a driving mechanism.

The vial oscillates along the vertical axis through the vials, with frequency in the range 13–20 Hz and amplitude of 30 mm. Impact speeds of the balls at 17 Hz frequency are 2·6–3·8 m/s (criterion "a") and the impact frequency of each ball is close to the movement frequency (criterion "b").[28] A dynamic compensation of inertial forces (becoming particularly critical for scaling-up the mill capacity) is provided by 4 + 4, counter-acting, pre-loaded springs, to fulfill the requirement of criterion "c".

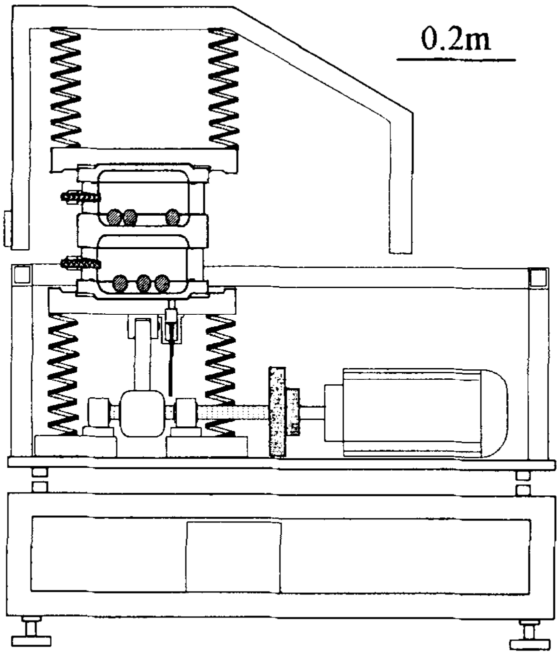

Fig. 1. Section view of the high-energy high-capacity mill (HCM).

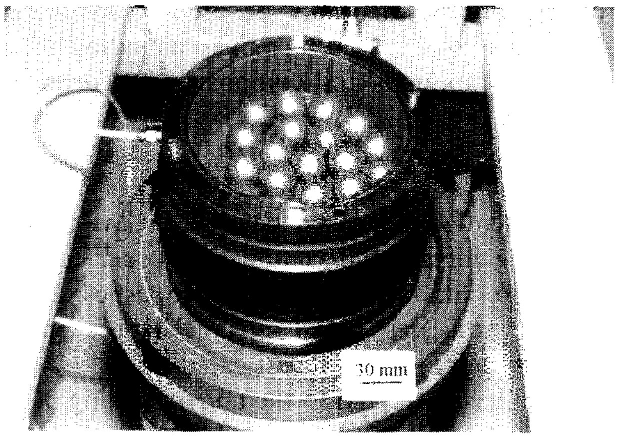

Fig. 2. Steel vial and balls being prepared for milling in the HCM.

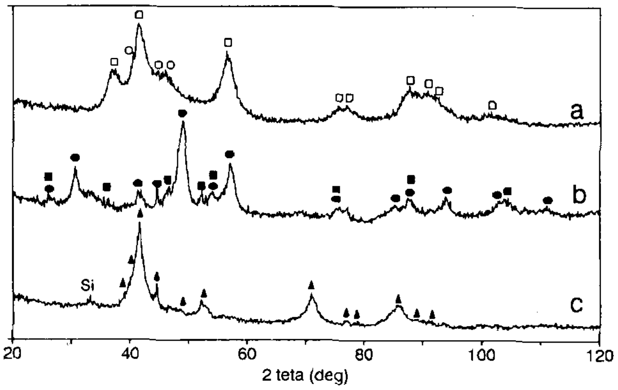

Fig. 3. XRD patterns for milled (in the HCM): (a) W and C for 19 h [WC (□); W_2C (○)]; (b) Mo and Si (1:2 atomic) for 18 h [β-$MoSi_2$ (●); α-$MoSi_2$ (■)]; (c) Si and C for 8.5 h [SiC (▲)].

The compensation of inertial forces allows an easy scale-up of the mill capacity (actually 1 kg of powders to be processed), by providing: (1) an increase in the size of the vial; and (2) design of the spring system to withstand the increased loads.

Experiments were performed to assess the ability of HCM to perform the synthesis of materials described in Section 2, such as silicon carbide, tungsten carbide and molybdenum disilicide.

Elemental powder (+99%, 30–60 μm, Si in pieces of some cm) mixtures of Si or Mo or W and graphite (stoichiometric proportions) were milled at room temperature in the HCM, using BPR 20:1–15:1, ϕ 25·4 mm carbon steel balls and a charge weight 100–130 g. Powders were introduced in the vial and sealed under Ar. Silicon carbide (SiC, rhombohedral, JCPDS 22-1316) and molybdenum disilicide ($MoSi_2$, mostly hexagonal β-$MoSi_2$ with a small amount of tetragonal α-$MoSi_2$) are both obtained by grinding for less than 10 h and 20 h, respectively. Complete tranformation (Fig. 3) of W and C to hexagonal WC (JCPDS 25-1047) was obtained (with a weak amount of W_2C) after 19 h milling. After sintering, the presence of W_2C was no longer detected.

To perform an estimation of the processing costs, it is first necessary to estimate the energy required. The maximum specific (per unit weight of powder produced) energy available in the HCM would be given by: $E_{av} = E_c\, 2ft/m = 1/2\, v^2\, 2ft$ BPR, where m is the powder mass, f the mill frequency, t is the milling time required to complete the synthesis, BPR is the ball to powder weight ratio, and $E_c = N\, 1/2 m_b v^2$ is the kinetic energy (of N balls, travelling with speed v and each having mass m_b).

In common working conditions ($f = 17$ Hz, BPR = 10–20, $t = 10$ h and $v = 2{\cdot}6$–$3{\cdot}8$ m/s, such as shown above for the mechanosynthesis of nanophase carbides and silicides), E_{tot} can be evaluated within 20 and 50 kWh/kg. The effective energy required (E_{req}), taking into account a restitution coefficient of the impact and the effective impact frequency and velocity for each ball (lower than f and v), would be about $0{\cdot}2$–$0{\cdot}3 \times E_{tot}$. Considering, for example, the synthesis of nanophase carbides and silicides reported above (requiring BPR = 20, ball weight = 2 kg and $R = 25.4$ mm, $t = 10$ h, charge weight 100 g), E_{req} is less than 5 kWh/kg (also in agreement with experimental data on the electric power absorption of the mill).

Such an evaluation of energy requirements, allows to estimate the transformation cost (energy plus maintenance and consumables of the mill) to produce nanophase materials to be below about $1 (US) per kg.

Table 1. Results obtained in the consolidated (HIP) Fe/Fe_3C (85 vol%) and Fe/Al_2O_3 (75 vol%) composites obtained by mechanosynthesis

Sample	HIP cycle (°C/MPa)	Relative density (%)	Microhardness ($HV_{0.5}$)	Hardness (HRA)	Indentation toughness (*Kc*) (MPa $\sqrt{m}$)
Fe/Al_2O_3 75 vol%	1000/200	100	1492	89	6·7
	1150/200	100	848	83	No cracks
Fe/Fe_3C 85 vol%	950/100	100	950	84.5	6·4
	600/150	98	1050	87	4·6

4 PROPERTIES OF CONSOLIDATED NANOCERMETS

The properties of fully dense solids were investigated for mechanosynthesized Fe/Al_2O_3 and Fe/Fe_3C nanocomposites. Alumina-based cermets have been extensively studied since the 1950s.[29] The combination of metal and ceramic toughens the brittle phase (ceramic) by using a ductile phase (metal) and should improve the brittleness and reliability of ceramics.

The Fe/Al_2O_3 (75 vol%) nanocomposites were obtained in the HCM (Section 2·4) using a mixture of starting powders (hematite, aluminium and alumina) of 50 g, which were introduced in the vial together with the grinding balls (2 kg, giving a ball to powder ratio of 40:1), the vial was then sealed, evacuated and filled with Ar.[21] The powders were mixed in stoichiometric proportions (an excess of alumina was used to reach 75 vol%) according to the reaction:

$$Fe_2O_3 + 2Al + 0{\cdot}66Al_2O_3 \rightarrow 1{\cdot}66Al_2O_3 + 2Fe \quad (4)$$

Hot isostatic pressing (HIP) was performed by forming green cylinders (ϕ 5 × 20 mm, by cold isostatic pressing (CIP) at 300 MPa of powders) which were encapsulated in low carbon steel cans.

The reaction was almost completed after 2 h milling, but it was prolonged to 8 h to also complete crystal size refinement. The XRD patterns clearly showed the main phases present to be α-Al_2O_3 and iron with crystal sizes of 12 and 15 nm, respectively. Consolidation by CIP/HIP (HIP cycles in Table 1, performed by heating and cooling from temperature in 30 min, and holding at temperature/pressure for 60 min) gave materials with slightly increased crystal sizes (below 40 nm for both the phases, for the HIP cycle at 1000 °C), which, however, remained in the nanoscale range.

The microstructures obtained in the consolidated material reveal a high level of intermixing of the ceramic (alumina, dark zones in Fig. 4) and metal (white zones in Fig. 4) phases. Table 1 shows that full densities were obtained even at 1000 °C, with an interesting combination of hardness and toughness. Such properties can even be compared to, and are not far from, the more sophisticated Sialon ceramics[30] used as cutting tool materials.

The synthesis of Fe/Fe_3C (85 vol%, corresponding to 5·7 wt% C) composites was performed in the

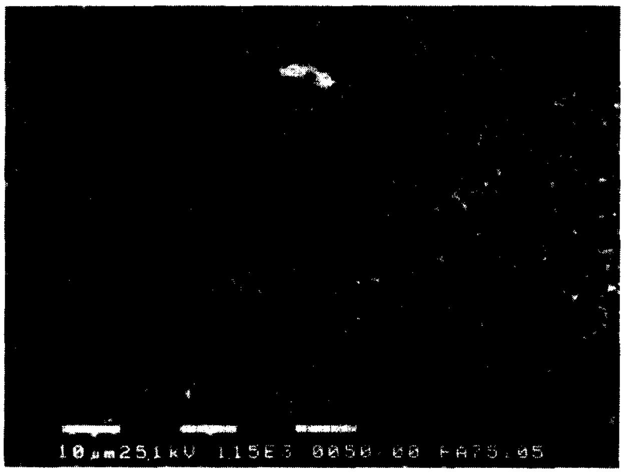

Fig. 4. SEM image of Fe/Al_2O_3 (75 vol%) nanocermet HIPed at 1050 °C/200 MPa.

Fig. 5. SEM image of Fe/Fe_3C (85 vol%) nanocermet HIPed at 950 °C/100 MPa.

HCM.[31] Starting materials were iron and graphite powders (100 g) which were introduced in the vial together with the grinding balls (2 kg, giving a ball to powder ratio of 20:1), the vial was then sealed, evacuated and filled with Ar. Cementite Fe_3C is already present after 5 h milling, the reaction being complete with the formation of the composite containing 85 vol% cementite after 10 h. The crystal size of Fe_3C was 18 nm. Powders were then consolidated, as in the previous case, by CIP/HIP, using the same methodology.

The consolidated samples showed a low extent of crystal growth, giving rise to a crystal size of ~50 nm at most, after a HIP cycle at 950 °C for 1 h. This notwithstanding the fact that the Fe–C eutectic is just about 200 °C above. The phases present appear to be iron and cementite (XRD). The microstructural observation (Fig. 5) reveals a fine dispersion of cementite particles (dark zones) in the iron matrix.

Fully dense solids were obtained at temperatures as low as 600 °C (Table 1). The hardness levels reached are very high, considering also that the samples were in the as-HIPed state. Toughness values are modulated by the HIP temperature. A particularly interesting combination of properties is reached, with hardness in the range 84·5–87 HRA and indentation toughness Kc in the range 4·6–6·4 $MPa\sqrt{m}$. Such properties can even be compared with some grades of cemented WC–Co carbides.[32]

5 CONCLUSIONS

Mechanical alloying and its evolution into the various processes, such as mechanosynthesis, has been shown to be capable of producing via solid state, almost room temperature, processing a wide variety of ceramic and composite materials having nanophase structures, also from the elemental powders (or compounds).

The method is promising at production scale for the costs and quantities which can be processed. Nanophase bulk solids obtained, such as nanocermets, exhibit improved and competitive mechanical properties.

ACKNOWLEDGEMENTS

This work was supported by the EEC, contracts SC1-CT91-0668/ERBCHBGCT920020, and MURST/CNR and CSGI grants.

REFERENCES

1. BENJAMIN, J. S., *Metall. Trans.*, **1** (1970) 2943.
2. DE BARBADILLO, J. J., *Key Eng. Mater.*, **77–78** (1993) 187.
3. BOLDYREV, V. V., *J. Chimie-Physique*, **83** (1986) 821.
4. GLEITER, H., *Prog. Mater. Sci.*, **33** (1989) 223.
5. CHOKSHI, A. H., *Mater. Sci. Eng.*, **A166** (1993) 119.
6. SCHAFFER, G. B. & McCORMICK, P. G., *Metall. Trans.*, **21A** (1990) 2789.
7. MATTEAZZI, P. & LE CAËR, G., *J. Am. Ceram. Soc.*, **75** (1992) 2749.
8. STEINIKE, U., KRETZSCHMAR, U., EBERT, I., HENNIG, H. P., BARSOVA, L. I. & JURIK, T. K., *Reactivity of Solids*, **4** (1987) 1.
9. BEGIN-COLIN, S., LE CAËR, G., MOCELLIN, A. & ZANDONA, M., *Phil. Mag. Lett.*, **69** (1994) 1.
10. MATTEAZZI, P. & LE CAËR, G., *J. Am. Ceram. Soc.*, **74** (1991) 1382.
11. LE CAËR, G., MATTEAZZI, P. & BAUER-GROSSE, E., Int. Patent WO 9001016, 21/7/1989, Pr. 22/7/1988.
12. MATTEAZZI, P. & LE CAËR, G., *J. Alloys & Compounds*, **187** (1992) 305.
13. MATTEAZZI, P., MIANI, F. & LE CAËR, G., *J. Hard Mater.*, **2**(3/4) (1991) 171.
14. MATTEAZZI, P. & LE CAËR, G., *Proc. Adv. Mater.*, **1** (1991) 135.
15. BOLDYREV, V. V., LYAKHOV, N. Z., PAVLYUKHIN, YU. T., BOLDYREVA, E. V., IVANOV, E. YU. & AVVAKUMOV, E. G., *Sov. Sci. Rev. B. Chem.*, **14** (1990) 105.
16. ELLIOT, I. C. & JACK, G. A., *Structural Applications of Mechanical Alloying*, ed. F. H. Froes & J. J. de Barbadillo. ASM International, OH, USA, 1990, p. 15.
17. WOLSKI, K. & THEVENOT, F., Ecole des Mines de Saint-Etienne, to be published.
18. POPOVICH, A. A., REVA, V. P. & VASILENKO, V. N., *J. Alloys & Compounds*, **100** (1993) 143.
19. SCHAFFER, G. B. & McCORMICK, P. G., *Metall. Trans.*, **22A** (1991) 3019.
20. MATTEAZZI, P., MIANI, F. & BASSET, D., *Nanostruct. Mater.*, **2** (1993) 355.
21. MATTEAZZI, P., ALCALÀ, M. D., BASSET, D., OSSO, D., LE CAËR, G., BEGIN-COLIN, S. & MOCELLIN, A., *PM '94 World Congress*, Paris, 6–9 June 1994. SF2 M, Paris, 1994, Vol. 3, pp. 1815–18.
22. OSSO, D., LE CAËR, D., BEGIN-COLIN, S., MOCELLIN, A. & MATTEAZZI, P., *J. De Physique IV, Coll. C7*, **3** (1993) 1407.
23. OSSO, D., TILLEMENT, O., LE CAËR, G., MOCELLIN, A. & MATTEAZZI, P., *Ceramics: Charting the Future*, ed. P. Vincenzini. Techna, Italy, 1995, pp. 1375–81.
24. MATTEAZZI, P., LE CAËR, G. & BAUER-GROSSE, E., European Patent No. EP 0454522A1, 30/10/91 (Pr. FR 9004820, 13/4/90).
25. TAKACS, L., *Mater. Lett.*, **13** (1992) 119.
26. McHARGUE, C. J., SKALD, P. S., FARLOW, G. C., PEREZ, A. & MAREST, G., *J. Mater. Res.*, **6** (1991) 2145.
27. BASSET, D., MATTEAZZI, P. & MIANI, F., *Mater. Sci. Eng.*, **A168** (1993) 149.
28. BASSET, D., MATTEAZZI, P. & MIANI, F., *Mater. Sci. Eng.*, **A174** (1994) 71.
29. *Cermets*. Reinhold Publishing Corp., New York, 1960.
30. *ASM Engineered Materials Reference Book*. ASM International, Metals Park, OH, USA, 1989.
31. MATTEAZZI, P., BASSET, D., ALCALÀ, M. D., LE CAËR, G. & BEGIN-COLIN, S., *PM '94 Powder Metallurgy World Congress*, Paris, 6–9 June 1994. SF2 M, Paris, 1994, Vol. 1, pp. 463–6.
32. BROOKES, K. J. A., *Handbook of Hardmetals, 4th edn.* International Carbide Data, UK, 1987.