Vol 10 Suppl., July 2001
1009-1963/2001/10(Suppl.)/0S31-05
Chinese Physics
© 2001 Chin. Phys. Soc.
and IOP Publishing Ltd

NANOSTRUCTURED AND AMORPHOUS MATERIALS BY MECHANICAL ALLOYING *

C. POLITIS[a)b)†]

[a)] *Institut für Nanotechnologie, Forschungszentrum Karlsruhe, Postfach* 3640, 76021 *Karlsruhe, Germany*

[b)] *School of Engineering, Engineering Science Department, University of Patras,* 26500 *Patras, Greece*

(Received 11 February 2001; revised manuscript received 14 May 2001)

Mechanical Alloying is particularly attractive because it can be used to process structurally uniform and isotropic bulk quantities of powdered materials that have a fine length scale. Furthermore, it appears to be applicable to many combinations of elements. Here experimental results regarding the synthesis and characterization of several binary and ternary nanocrystalline and amorphous alloys of Ti, Zr, Hf, V, Nb and Fe with other transition elements and with B, C and Si are reported. The nanocrystalline and amorphous powders, with effective particle size between 7 and 30nm, were prepared by mechanical alloying in a high-energy ball-mill using commercial elemental powders and/or alloy powder.

Keywords: nanostructured materials, amorphous alloys, mechanical alloying
PACC: 6146, 6155H

I. INTRODUCTION

In the past 50 years a large number of microcrystalline and amorphous metallic alloys have been obtained by several techniques of quenching from the vapor[1] or the liquid state.[2] The disadvantage of these methods is that only thin films, or splats of foils can be prepared as a result of the necessity of a fast heat transfer to prevent crystallization.

The most commonly utilized industrial techniques are melt spinning for the continuous fabrication of uniform amorphous metallic ribbons and other rapid-solidification-rate methods for producing metal powders. In research sputtering, splat quenching, ion implantation, electrodeposition, chemical deposition, laser glazing, solid state reaction and gas-phase synthesis are often employed.

Intense deformation during repeated mechanical mixing, cold-welding, fracturing, and rewelding of ultrafine powders and microcompacts in high-energy ball mills without lubricants produces mechanically formed alloys.[3] Mechanical alloying used in the range of powder blending for the production in powder metallurgy can produce alloys of elements, which cannot be formed by solid state reactions and sintering, melting or quenching from the liquid state. In this way, it is possible to develop alloys with properties that differ considerably from those of the correspnding sintered, molten or quenched materials.

It was also reported that amorphous or partially amorphous structures without a detailed analysis of the fine length scale of the alloys were obtained when elemental powder mixtures of Y–Cu or Gd–Co were mechanically alloyed.[4,5] The first absolutely structurally amorphous alloy prepared by mechanical alloying was obtained by Koch *et al.*[6], i.e. for samples of $Ni_{60}Nb_{40}$.

Early examples of successful preparation of amorphous alloys by mechanical alloying were also reported for Nb–Ge–Al,[7] Ni–Ti[8] and $Ti_{1-x}Cu_x$ ($0.10< x \leq 0.87$).[9] The synthesis and crystallization behavior of ternary Ti–Pd–Cu alloys were investigated and compared with liquid-quenched materials of the same compositions.[10] Complete amorphization of Ti–Pd alloys was demonstrated for the first time.[11] By ball milling, several mixtures of early and late transition metals were also mechanically alloyed.[12,13]

Nanocrystalline materials are a new class of disordered solids obtained by introducing such a high density of defect cores that 50% or more of the atoms are situated at the grain boundaries.[14] Such nanocrystalline materials typically have average grain sizes of 2 to 50nm and can exhibit properties that are very different from those of conventional materials. Nanocrystalline materials can be also synthesized by mechani-

*Project supported by the International office of the German Ministry of Education and Research, the Research Committee of the University of Patras, the Greek General Secretariat of Research and Technology and by the European Social Fund under the PENED '99 project 99ED52.

†Correponding auther. E-mail address: c.politis@des.upatras.gr

cal alloying.[10,15–17] Recently, it was reported[18] that nanocrystalline and amorphous phases can also be prepared by mechanical alloying in immiscible binary systems like W–Cu.

Mechanically alloyed amorphous and nanocrystalline clusters and powders are of considerable interest at present. A major source of this interest is the promise of fascinating bulk amorphous or nanocrystalline materials, which are structurally uniform and isotropic.

This paper will discuss the synthesis and characterization of nanocrystalline structures produced by mechanical alloying of Ti, Zr, Hf, V, Nb and Fe with other transition metals and with B, C and Si.

II. EXPERIMENTAL PROCEDURES

Two methods of alloy formation, mechanical alloying and liquid quenching, were utilized in this work, for comparison of both techniques and results. For the liquid quenching studies, alloys buttons were prepared by repeated arc melting in high-purity (99.999%) static Ar gas, first scoured with molten Zr.

Amorphous $Hf_{35}Ni_{65}$ splats were formed from levitation-melted (splat cooling) samples (∼500mg), which were quenched (with quenching rates of $5\times10^6 Ks^{-1}$) between double Cu–Be pistons, producing foils of 20–30μm in thickness and 20–30mm in diameter.

For the studies, fine powders of Ti, Zr, Hf, V, W, Fe, Co, Ni and Cu (99.95 to 99.99%, 325 mesh), and B, C and Si (99.999%, 325 mesh) were used as starting materials. Powder mixtures of appropriate composition were mixed for several minutes using a glass rod in a small vial prior to milling.

The powders were hand-mixed in a glove box, then loaded into a high energy ball milling apparatus (Spex 8000 or Fritsch Pulverisette 5). Milling was carried out alternatively in a hardened tool steel vial or in a tungsten carbide vial (WC+6% Co). The volumes of the two vials were identical (80ml). The balls used for milling were made of WC+6% Co. Balls of 3, 6, 8 and 10mm diameter were used. The best results were obtained using balls of 8 and 10mm diameter. The ball-to-powder weight ratio varied between 2:1 and 12:1.

In order to prevent oxidation, the ball mill was sealed under dry argon (≥99.999%) inside a glove box. For this purpose the respective vials of tool steel or WC were fitted with O-rings made of Viton and/or cooper. Leakage was checked and found to be less than 5×10^{-9} mbar lt s^{-1} at an overpressure of 1.1 bar of He.

The vials were always loaded in the glove box at an inside overpressure of 1000 mbar of purified dry argon. In air the ground powder was found to already have picked up considerable quantities of oxygen and nitrogen after 5–10s duration of the grinding process. This could be deduced from the immediate reduction of the pressure during milling in a vial sealed in open air. The tendency of the powders to purl was controlled. Periodically (5–15min), the vial was rotated by 90° in order to obtain thorough and uniform mixing. Less frequently (1/2–2 h) it was opened in the glove box to clean accumulated sample material (agglomeration and sticking) from the balls and wall of the vial.

The milling process was periodically interrupted every hour and, at glove box conditions, small amounts of mechanically alloyed powder was removed for X-ray diffraction analysis. In addition, small quantities (50mg) of the alloys were prepared for chemical and powder screening analysis, scanning electron microscopy, differential thermal analysis or differential scanning calorimetry.

The specimens for X-ray investigations were prepared in a glove box by applying a layer of screened powder to a plexiglass sheet using a small amount of high vacuum silicon grease as a binder. X-rays diffractograms were determined using a vertical and a horizontal powder diffractometer with Cu$K\alpha$ radiation (λ=0.15418nm) or Co$K\alpha$ radiation (λ=0.17902nm) without a monochromator.

Differential thermal analysis studies were also performed in a Netzsch simultaneous thermal analysis STA 409 apparatus on 100 mg powder samples. An equal mass of Al_2O_3 (99.99%) served as reference in the 20K/min scans, that were conducted in a static He atmosphere. For thermometry, Pt 10% Rh–Pt thermocouples were used with both analog and digital recording of data.

III. RESULTS AND DISCUSSION

Figures 1–3 show the gradual formation of nanocrystalline and amorphous structures in alloys of $Hf_{35}Ni_{65}$, $Ti_{50}Ni_{50}$ and $V_{50}Ni_{50}$. After a few hours of processing, a broad diffraction peak appears near 2θ=42° for $Hf_{35}Ni_{65}$ and near 2θ=44° for $Ti_{50}Ni_{50}$ and $V_{50}Ni_{50}$. These broad peaks are superimposed by relatively sharper Bragg peaks characteristic of the

nanocrystalline elemental phases.

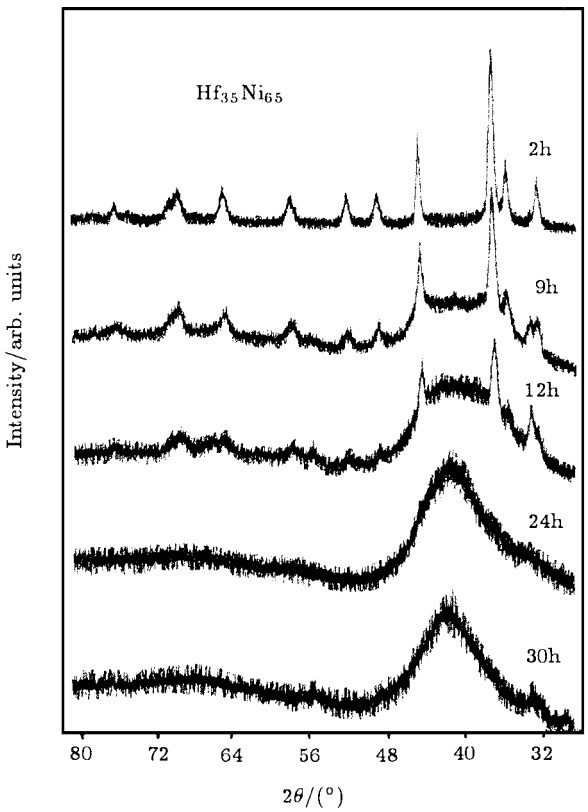


Fig.1. X-ray diffractograms (Cu$K\alpha$ radiation) of $Hf_{35}Ni_{65}$ alloy. After 24h of ball milling a completely amorphous structure was observed.

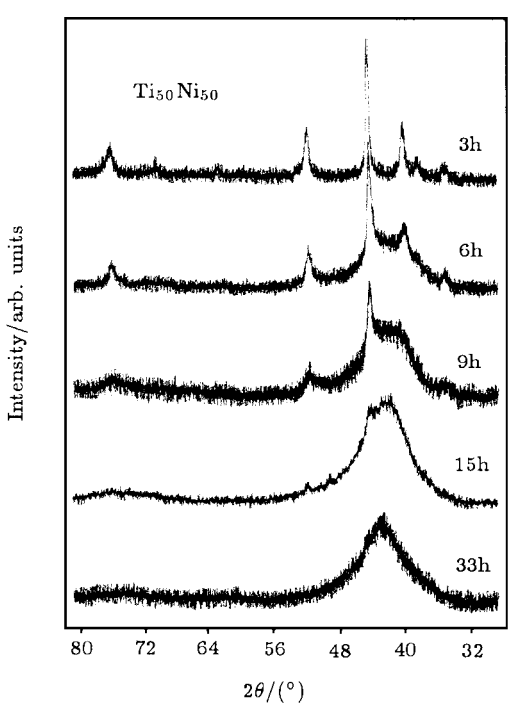


Fig.2. X-ray diffractograms (Cu$K\alpha$ radiation) of $Ti_{50}Ni_{50}$ alloy. After 33h of ball milling a completely amorphous phase is observed.

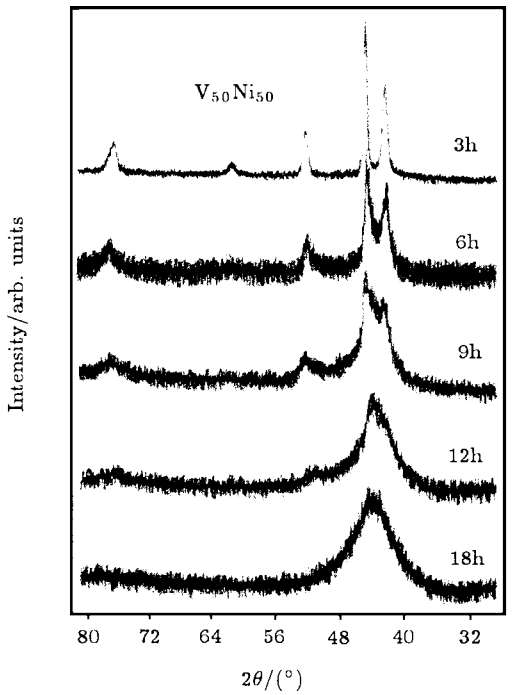


Fig.3. X-ray diffractograms of $V_{50}Ni_{50}$ alloy.

With increasing milling time powders gradually become amorphous. In the $Hf_{35}Ni_{65}$ alloy after 24h of grinding, a completely amorphous structure was observed. For $V_{50}Ni_{50}$ and $Ti_{50}Ni_{50}$, finally, after 18h and 33h of processing, respectively only the broad diffraction peak near 2θ=44°, followed by a still broader but very weak diffraction peak near 2θ=76°, are seen.

It must be noted that the very strong peak at 2θ=42° or 2θ=44° in the initial spectrum of the starting material is a superposition of the two most intense elemental reflections of the (101) reflex of the hcp α-Ti, α-Zr and α-Hf, the (110) reflex of the bcc V and the (111) reflex of the fcc Ni.

Consequently, it is not surprising that as the amorphous state is generated, its first reflection maximum is created closely to these diffraction angles. This first peak, representing the contribution of the nearest-neighbor atoms can shift to higher or lower 2θ values with increasing partner concentration.[9] This pattern is characteristic of amorphous alloys. Generally, a similar behavior was previously observed for amorphous alloys of Ti–Cu,[9] Ti–Pd[9] and Ti–Cu–Pd.[13,19]

The widths of the primary diffraction maxima provide for an additional characterization for the ma-

terials. To obtain the relationship between the effective particle size (mean crystallite dimension normal to the diffracting planes) and X-ray line broadening, the Scherrer equation was used. The half-maximum line breadth of the first diffraction peak was corrected for Cu or Co$K\alpha$-doublet separation and instrumental broadening.

Figure 4 shows the effective particle size of $Ti_{50}Ni_{50}$, $Hf_{35}Ni_{65}$ and $V_{50}Ni_{50}$ mechanical alloying powders and nanostructured materials as a function of the milling time. Initially, there is a rapid decrease in size, in the course of which the starting materials are bonded, thinned and fractured repeatedly.

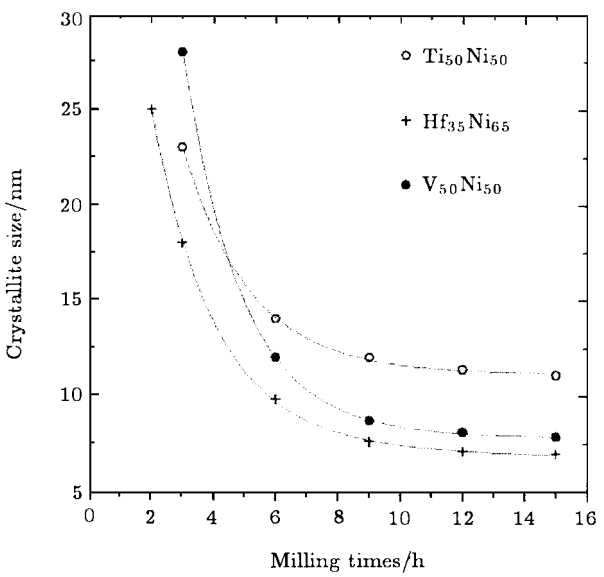


Fig.4. Effective particle size of $Ti_{50}Ni_{50}$, $Hf_{35}Ni_{65}$ and $V_{50}Ni_{50}$ mechanically alloyed powders as a function of milling time. In 4h of mechanical alloying the effective particle size has dropped between 15 and 25nm.

A more gradual refinement follows, during which the mixing occurs on a much more microscopic scale, greatly assisted by the mixing energy, point defects, dislocations, alloying etc resulting from mechanical alloying. As the last step, a limiting size is approached, asymptotically with a diameter of 7–11nm for the amorphous state.

The particle size is much larger in $Ti_{50}Ni_{50}$ alloys, which remain nanocrystalline-amorphous in the mixed-state for a long period (6–8h) of milling. However, the macroscopic physical form of the powders itself consists of larger clusters, nanocompacts, and agglomerations.

Nanocrystallinity with an effective particle size of 14–30nm was observed in the early state (2–5h) of repeated deformation processing. The fully amorphous structure shows up after several hours (>8h for $Ti_{50}Ni_{50}$) for an equivalent effective particle size of about 7 to 11nm.

In order to distinguish between the processes of mechanical alloying and liquid quenching, a series of Ti–Cu and Hf–Ni alloys have been investigated. We found that, mechanical alloying, in contrast to liquid quenching, leads to the amorphous state in a wide concentration region of the Ti–Cu, Ti–Ni, Hf–Ni and V–Ni systems. These results indicate that the mechanisms of amorphization and crystallinity are different for liquid quenching and mechanical alloying.

Table 1 shows the crystallization temperature T_{x1} for several amorphous alloys prepared by ball milling. The milling time to establish the amorphous state of these materials lies between 3h for the ternary alloy $Ti_{50}Pd_{35}Cu_{15}$ and 18h for the binary V–Ni alloys. A relatively high crystallization temperature of 1050K is observed for the amorphous ternary alloy $Ti_{40}Ni_{40}Si_{20}$ and 1035K for the multi-component amorphous alloy $Fe_{42}Cr_{18}Mo_{16}W_6C_{18}$.

Table 1. Formation and crystallization temperatures of some investigated Ti–, Zr–, Hf–, V– and Fe– based amorphous alloys by ball milling.

Amorphous Alloys, Obtained with MA	Milling Time for Amorphous State /h	Crystallization Temperature T_{x1}/K
$Ti_{15}Co_{85}$–$Ti_{80}Co_{20}$	6–9	740–845
$Ti_{40}Ni_{40}Si_{20}$	12	1050
$Ti_{40}Pd_{60}$–$Ti_{85}Pd_{15}$	6	620–750
$Ti_{50}Pd_{35}Cu_{15}$	3	815
$Ti_{10}Cu_{90}$–$Ti_{90}Cu_{10}$	6	605–680
$Ti_{70}Ni_{30}$–$Ti_{30}Ni_{70}$	12–33	710–760
$Zr_{65}Cu_{35}$	6	820
$Zr_{75}Rh_{25}$	9	678
$Zr_{50}Fe_{50}$	16	879
$Hf_{65}Fe_{35}$	6	870
$Hf_{10}Co_{90}$–$Hf_{85}Co_{15}$	6	740–833
$Hf_{10}Ni_{90}$–$Hf_{85}Ni_{15}$	6–24	722–955
$Hf_{10}Cu_{90}$–$Hf_{85}Cu_{15}$	6	810–920
$V_{85}Ni_{15}$–$V_{50}Ni_{50}$	18–32	833–860
$Fe_{12}Ti_{72}Si_{16}$	12	880
$Fe_{40}Ni_{40}B_{20}$	16	733
$Fe_{77}B_{13}Si_{10}$	12	823
$Fe_{42}Cr_{18}Mo_{16}W_6C_{18}$	8	1035

X-ray analyses, EDAX, and chemical analysis have shown that contamination of the mechanically alloyed powders by abrasion of the balls is small and can be minimized to a low impurity level by choosing the right material for both the vial and balls. It

was found that when using a hardened tool steel vial and balls or tungsten carbide vial (WC+6% Co) and balls, the typical product powders contain less than 200 ppm Fe, 50 ppm Co, 100 ppm W, and less than 100 ppm C.

IV. CONCLUSION

Nanocrystalline and amorphous powders, of binary and ternary alloys of transition metals, can be produced by mechanical alloying. Comparison of mechanically alloyed nanostructured and amorphous materials with liquid-quenched alloys has demonstrated that both classes of materials exhibit very similar properties, e.g. crystallization temperatures and atomic structures.

There is an important difference regarding the mechanism of the process and the compositions formed amorphous alloys produced by liquid quenching and mechanical alloying. Liquid quenching methods function best for compositions near melting point minima like eutectics. In contrast mechanical alloying in some cases can amorphize alloys corresponding also to melting point maxima.[12]

An other significant difference is that, in comparison with liquid quenching, nanostructurization and amorphization by mechanical alloying process is a combination of several solid state mechanisms.

To consolidate such multicomponent powdered materials with ultrafine microcrystalline and/or amorphous structures, the techniques of hot pressing, hot isostatic pressing and dynamic shock waves compaction were used.[20]

As a matter of fact, the mechanical alloying method should be considered as a new by means of assembling many homogeneous amorphous and/or nanocrystalline materials which cannot be prepared by the conventional methods of liquid quenching.

ACKNOWLEDGEMENT

I would like to thank L. Deimling, W. Krauss, and V. Kapaklis for the technical assistance in the studies.

References

[1] Buckel W and Hilsch R 1952 *Z. Phys.* **132** 420

[2] Duwez P 1960 *J. Appl. Phys.* **31** 1136

[3] Benjamin J S 1970 *Metall. Trans.* **1** 2943

[4] Ermakov A E, Yurchikov E E and Barinov V A 1981 *Fiz. Metal. Metaloved.* **52** 1184

[5] Ermakov A E, Barinov V A and Yurchikov E E 1982 *Fiz. Metal. Metaloved.* **54** 935

[6] Koch C C, Cavin O B, McKamey C G and Scarbrough J O 1983 *Appl. Phys. Lett.* **43** 1017

[7] Politis C 1985 *Physica* B **135** 286

[8] Schwarz R B, Petrich R R and Saw C K 1985 *J. Non-Cryst. Solids* **78** 281

[9] Politis C and Johnson W L 1986 *J. Appl. Phys.* **60** 1147

[10] Politis C and Thompson J R 1987 in *Science and Technology of Rapidly Quenched Alloys* ed Tenhover L E T M and Johnson W L (Pittsburgh: Materials Research Society) **80** p 81

[11] Thompson J R and Politis C 1987 *Europhys. Lett.* **3** 199

[12] Thompson J R, Politis C and Kim Y C 1988 *Materials Science and Engineering* **97** 31

[13] Politis C 1988 *Zeitschrift f. Phys. Chemie Neu Folge* **157** 233

[14] Gleiter H 1981 in *Proc. of the Second Risφ International Symposium on Metallurgy and Materials Science* ed N. H. *et al* (Roskilde) p 15

[15] Hellstern E, Fecht H J, Fu Z and Johnson W L 1989 *J. Appl. Phys.* **65** 305

[16] Zang J S C and Koch C C 1990 *J. Mater. Res.* **5** 498

[17] Koch C C and Cho Y S 1992 *NanoStructured Materials* **1** 207

[18] Aboud T, Weiss B Z and Chaim R 1995 *NanoStructured Materials* **6** 405

[19] Politis C and Thompson J R 1986 in *Horizons of Powder Metallurgy Part I*, ed W. L. H. W. A. Kaysser (Freiburg: Verlag Schmid) p 141

[20] Krauss W, Politis C and Weimar P 1988 *Metal. Powd. Report* **43** 231