Vol 10 Suppl., July 2001
1009-1963/2001/10(Suppl.)/0S27-04
Chinese Physics
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NANOSTRUCTURED MULTI-COMPONENT MATERIALS BY MECHANICAL ALLOYING

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(Received 2 November 2000; revised manuscript received 4 May 2001)

We have shown that nanostructured multi-component materials like TaC, $Nb_{78}Ge_{22}$, $Mo_{70}Si_{20}B_{10}$, $Mo_{60}Os_{20}B_{20}$, $Ru_{52}Zr_6B_{42}$, $(NbC)_{20}Co_{80}$ and $(WC)_{80}$–$(Ti_{90}Cu_{10})_{20}$ with an effective length size reduced to atomic level (a few nanometers) can be produced by mechanical alloying of the elemental and/or alloy powders in a high-energy ball mill. All process steps and samples preparation for characterization were done under glove box conditions.

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

I. INTRODUCTION

Application of reinforced metallic and ceramic materials and composites has increased tremendously. Apart from aerospace industry, chemical, electrical, automobile and sports industries are big users, in one form or another, of multi-component materials.[1]

Very recently, applications of nanostructured multi-component materials focused on microelectronics. In the past decade, semiconductor industry grew very rapidly. In a research environment advanced methods of patterning reach a resolution of $\leq$10nm. According to the current state of the art, new developments of nanoscaled devices near the limit of the single electron transistor appear to be realistic.[2] Within the framework of this research and development situation, nanostructured materials are now on the top. The main reason is that if the relevant length scale and/or physical dimensions of a particle or microcompacts are reduced to atomic scale, the structural, electronic and other physical and mechanical properties may change greatly. A variety of methods, particularly mechanical alloying, can be used to prepare materials that have a fine length scale.

A very promising method for the production of powdered multi-component materials with ultrafine microstructures is the process of mechanical alloying. Intense strength of deformation during repeated mechanical mixing, cold welding, fracturing and rewelding of ultrafine powders and microcompacts in a high energy ball mill produce homogeneous nanostructured materials even of such elements which can be alloyed neither by diffusion and sintering nor by melting.[3]

In this study, we investigated a variety of binary and ternary alloys composed of TaC, $Nb_{78}Ge_{22}$, $Mo_{70}Si_{20}B_{10}$, $Mo_{60}Os_{20}B_{20}$, $Ru_{52}Zr_6B_{42}$, and multi-component materials like $(NbC)_{20}Co_{80}$ and $(WC)_{80}$–$(Ti_{90}Cu_{10})_{20}$.

II. EXPERIMENTAL PROCEDURES

The starting materials for the amorphous and/or nanostructured multi-component powder were fine elemental powders, typically 325 mesh. All powders were of $\geq$99.99% purity. The powders were hand-mixed, then loaded into a high-energy ball milling apparatus for processing in either a hardened steel or tungsten carbide vial with balls of the same material.

All ball milling was conducted in a glove box under Ar atmosphere ($\leq$5ppm N_2, O_2 and H_2O) in order to prevent oxidation of the powders. The vial was opened in the glove box periodically and cleaned to ensure thorough mixing of the components and extract small portions for X-ray and other analysis.

The progress of nanostructurization and amorphization was assessed by periodic (every hour) X-ray diffraction of sieved powder samples using a standard diffractometer with Ni-filtered Cu$K\alpha$ radiation (λ=0.15418nm) or Co$K\alpha$ radiation (λ=0.17902nm). For calculation of the crystallite size from the X-ray

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line broadening the Scherrer equation was used:

$$D = \frac{K\lambda}{\beta \cos\theta},$$

Here K is a constant that depends largely on the crystallite shape, the (hkl) indices, and the definitions taken for β and D. Values from 0.7 to 1.7 were assumed for K by different investigators.[4] It was shown that a K value of about 0.9 was reached when β was taken as the half maximum line width. Therefore, D is directly proportional to the wavelength λ in Å and inversely proportional to the pure diffraction broadening β and the cosine of the Bragg angle θ.

Determination of the pure diffraction width β constitutes the major effort associated with crystallite-size analysis.

In comparison with the X-ray diffractometry the effective particle size was determined by scanning electron microscopy, transition electron microscopy and atomic force microscopy. The amorph-crystalline state was also controlled by thermal analysis with a Netzsch STA 409 apparatus.

III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffractograms of $Mo_{70}Si_{20}B_{10}$ nanostructured materials after 1, 3 and 6h of ball milling respectively. Using elemental Mo, Si and B powders after 1h of the process, a complete new thermodynamically stable nanostructured (∼30nm) phase is formed.

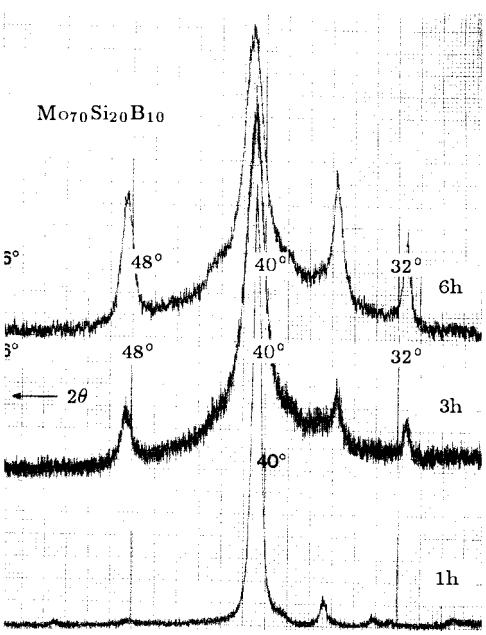


Fig.1. X-ray diffractogram of 1, 3 and 6h mechanically alloyed $Mo_{70}Si_{20}B_{10}$, starting from mixture of elemental powders.

Figure 2 shows the X-ray diffractogram of nanostructured $Nb_{78}Ge_{22}$ after 9h of ball milling with an effective particle size of d=3nm, which is in a good agreement with previous data.[3]

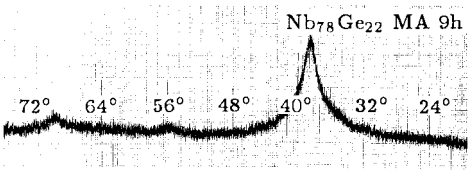


Fig.2. X-rays diffractogram of $Nb_{78}Ge_{22}$.

A series of experiments on the formation of nanostructured and amorphous ternary Mo–Os–B and Ru–Zr–B alloys, with starting materials the elemental Zr, Mo, Ru, Os and B has been performed. Figure 3 shows the diffractograms of semi-amorphous multicomponent $Mo_{60}Os_{20}B_{20}$ and of complete amorphous $Ru_{52}Zr_6B_{42}$ after 6h of ball milling. Both diffractograms give a good example of 'liquid - like' amorphous metallic alloys with the characteristic first and second broad diffraction maxima. In the case of $Mo_{60}Os_{20}B_{20}$ the maxima lies at 2θ=41° and 2θ=71°, and in the case of $Ru_{52}Zr_6B_{42}$, at 2θ=40° and 2θ=73°. The multi-component $Mo_{60}Os_{20}B_{20}$ sample has also contributions of nanocrystalline phases which are in the diffractogram just recognizable. The nanocrystall inity disappears completely after 9h of ball milling and the material becomes completely amorphous.

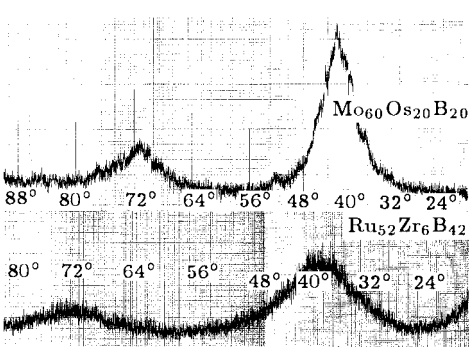


Fig.3. X-ray diffractograms of multi-component nanostructured $Mo_{60}Os_{20}B_{20}$ and amorphous $Ru_{52}Zr_6B_{42}$.

The carbides of transition elements like NbC, WC or TaC have as nanostructured materials a great potential of applications. Figure 4 shows the diffractograms of arc melted $(NbC)_{20}Co_{80}$ as starting material and also after 3 and 6h of ball milling. The ef-

fective particle size of nanocrystalline Co in these two component materials is 7nm after 3h and only 3nm after 6h of ball milling.

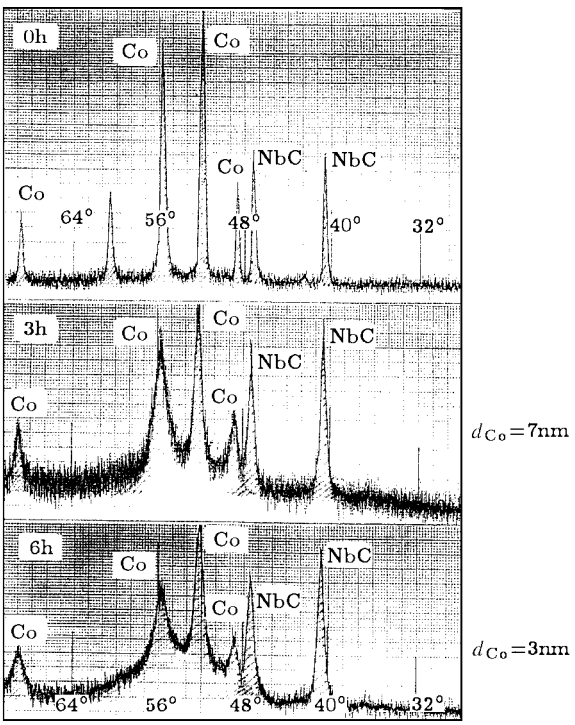


Fig.4. X-ray diffractograms of nanostructured multi-component $(NbC)_{20}Co_{80}$.

Figure 5 shows the diffractograms for the multi-component $(WC)_{80}$–$(Ti_{90}Cu_{10})_{20}$ after 3 and 6h of ball milling, respectively.

We can clearly see that if one of the metals in the mixture is brittle like Ti, the effective particle size becomes easy smaller. Here, after 3h of ball milling the particle size of Cu is 15nm and for Ti 12nm, respectively. As the process goes on and after 6h of treatment, we measure by the X-ray method 6nm effective particle sizes for Cu and 5 nm for Ti. These are the first steps for bonding of NbC and WC with nanostructured and amorphous Co and Ti-Cu alloys.

Figure 4 and 5 demonstrated that in the case of ball milling of multi-component materials some of the metals or alloys will develop separately to form amorphous or nanostructured phases. This can be important by processes with self-propagation to form nanostructured multi-component materials for microelectronic applications, on basis of 3D-quantum dots (metallic and semiconductive).

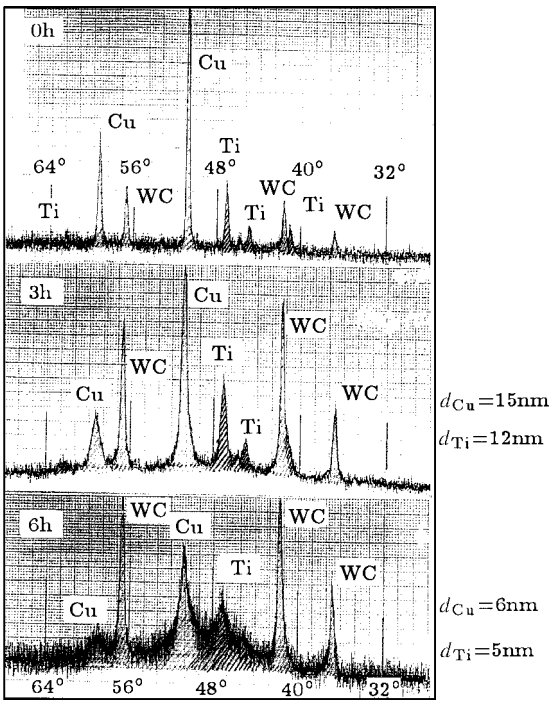


Fig.5. X-ray diffractograms of fine powder of WC, and elemental Cu and Ti powders, with the nominal composition of $(WC)_{80}$–$(Ti_{90}Cu_{10})_{20}$, after 0, 3 and 6h of ball milling.

We tried to nanostructure also pure single phase TaC (with nominal stoichiometry of C/Ta=0.995) as well. In Figure 6, the X-ray diffraction spectra of TaC are plotted versus increasing process time. After 2h of ball milling, significant reflexes appear that belong to α-WC (101) and (001). The α-WC phase is a contamination caused by the WC vial and balls.

The TaC after 45min of ball milling, however process started to show a smaller particle size. For TaC, a very small shift of the diffraction peaks to higher 2θ values was observed with ball milling time.

For comparison and calibration, investigations of nanostructured TaC by SEM, TEM, and AFM are shown in Figure 7. After 6h of ball milling, we found an effective particle size of 40nm by SEM (30kV), 8nm by TEM (200kV), and 12nm by AFM (taping mode). The difference between the various experimental methods is through the nature of the instrument used. The recognition and the resolution of the fine structure is better with 200kV TEM as with 30kV SEM. Good agreement has been found between measurements realized by TEM and AFM.

Among the processes with the highest potential for tailoring advanced materials, mechanical alloying techniques are of special interest because they offer great flexibility in the choice of constituent materials to be combined.[5]

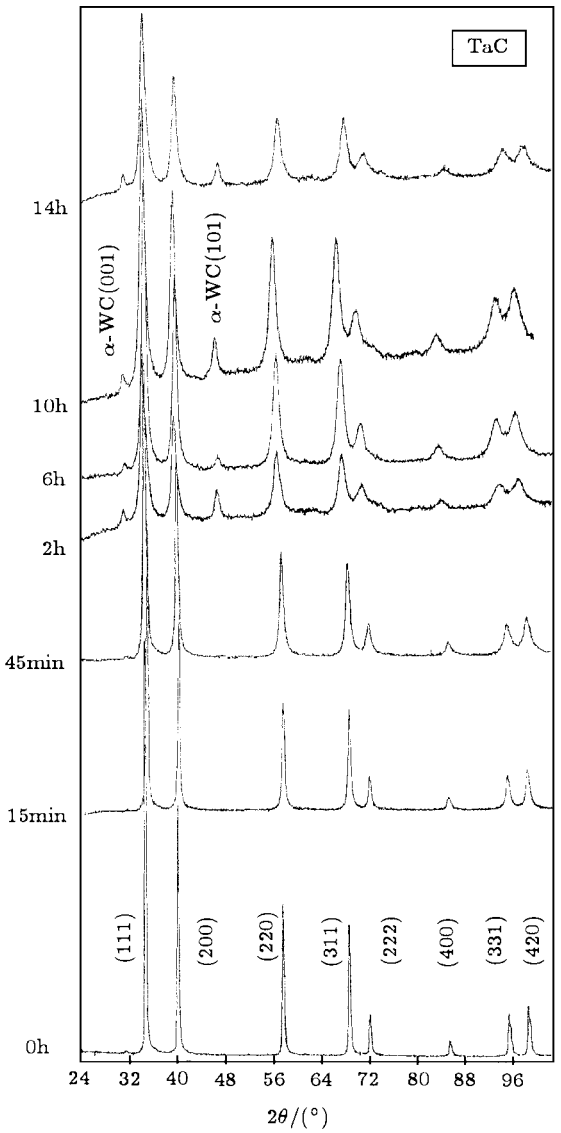


Fig.6. X-ray diffractogram of arc melted TaC, after 0–14h of ball milling.

IV. CONCLUSIONS

The results of the mechanical alloying show that although the borides $Mo_{60}Os_{20}B_{20}$ and $Ru_{52}Zr_6B_{42}$ can be amorphous, TaC, $Nb_{78}Ge_{22}$ and $Mo_{70}Si_{20}B_{10}$ form a nanostructured phase. The multi-component carbides $(NbC)_{20}Co_{80}$ and $(WC)_{80}$–$(Ti_{90}Cu_{10})_{20}$ develop simultaneous on the same sample an amorphous phase (Ti-Cu) and a nanocrystalline phase (Co, NbC or WC).

The synthesis of the above materials was examined in respect of the fabrication of reinforced composites and also as the first steps for application in nanoscaled electronic devices. We found that, mechanical alloying by ball milling is a very useful tool for the fabrication of such nanostructured multicomponent materials with an effective length scale reduced to atomic level.

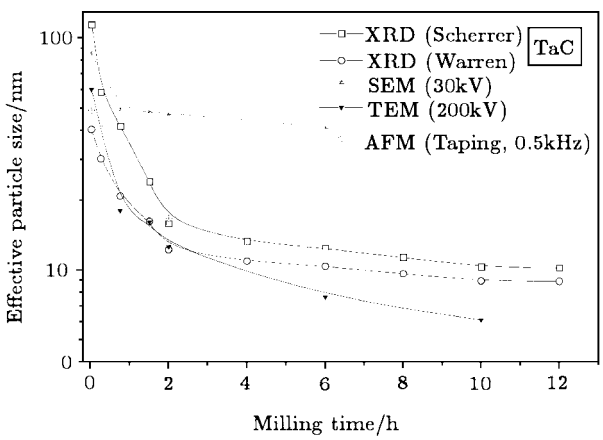


Fig.7. Effective particle size of TaC versus milling time. Comparison of XRD, SEM, TEM and AFM characterization methods for the effective particle size. Good agreement between AFM and TEM.

ACKNOWLEDGEMENT

This work has been supported by the Forschungszentrum Karlsruhe, the International Büro of the Bundesministerium für Bildung und Forschung in Bonn, Germany, the Research Committee of the University of Patras, the Greek General Secretariat of Research and Technology and the European Social Fund under the PENED '99 project 99ED52.

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