

Ti-Y₂O₃ Composites with Nanocrystalline and Microcrystalline Matrix

MAREK KRASNOWSKI and JAN RYSZARD DĄBROWSKI

Mechanical milling of a Ti-2 pct Y₂O₃ powders mixture led to the synthesizing of a composite powder with a nanocrystalline Ti matrix having a mean crystallite size of 19 nm. Both the nanocomposite powder prepared through milling and the initial mixture of powders were consolidated by hot pressing under the pressure of 7.7 GPa at the temperature of 1273 K (1000 °C). The transmission electron microscopy (TEM) investigations of the bulk sample produced from milled powder revealed that Y₂O₃ equiaxial particles of less than 30 nm in size are distributed uniformly in the Ti matrix with a grain size in the wide range from 50 nm to 200 nm. The microhardness of the produced nanocrystalline material is 655 HV0.2, and it significantly exceeds the hardness of the microcrystalline material (the consolidated initial mixture of powders), which is equal to 273 HV0.2. This finding confirms that reducing the grain size to the nanometric level can have a beneficial influence on the hardness of titanium alloys. Dispersion hardening also contributes to the hardness increase.

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I. INTRODUCTION

IN recent years, the increased requirements of modern medicine with respect to biomaterials have impelled scientists to apply new technological solutions for obtaining materials that better fulfill their purposes. The unique properties of titanium—low density, good resistance to corrosion, and excellent biocompatibility—have been used for many years. Titanium alloys are considered the most promising metallic biomaterials because of their good metallic properties combined with biocompatibility with biologic tissue.^[1–5] Titanium and its alloys are applied widely in medicine in the production of reconstructive elements for osteosyntheses and endoprosthesis surgery.^[1–5] Beta-phase alloys are currently among the most promising groups of titanium alloys. Much research concentrates on modifying the mechanical and tribological properties of beta-phase titanium alloys.^[6–9] Numerous investigations have been carried out on the production of titanium alloys of nanometric structures and structures reinforced by introducing dispersive particles to improve the mechanical properties.^[10–17]

Nanocrystalline materials exhibit exceptionally advantageous properties, which are not reached by advanced materials of typical microstructures. Among such properties are the following: hardness, strength, abrasion resistance, tribological properties, creep resistance, plasticity, embrittlement temperature, corrosion

resistance, antibacterial and sterile properties, diffusion, or thermal expansion.^[18,19] Because of the favorable properties of nanocrystalline materials, their production technologies are improved systematically. Titanium alloys are interesting materials for biomedical applications in the production of different kinds of implants.^[5] This area also necessitates the improvement of the functional characteristics of the alloys by comminuting their structure to the nanometric level. The techniques applied for this purpose include, among others, powder ball milling and severe plastic deformation of solid materials. The powder ball milling method is also applied to introduce dispersive particles, *e.g.*, particles of yttrium oxide, which enhance hardness, strength, and structural stability at increased sintering temperature.

Most applications of nanocrystalline materials require their solid forms, so powders should be consolidated after milling. One should note that applying a high temperature of consolidation may lead to grain coarsening and loss of the nanocrystalline structure. That is why consolidation of nanocrystalline materials is both an important and difficult task to perform. The literature shows that applying the high-pressure hot-pressing technology can retain the nanocrystalline structure of powders during consolidation.^[19–21]

In the course of the current investigation, Ti-Y₂O₃ composites of nanocrystalline and microcrystalline structures were produced using the powder consolidation method. The consolidated materials were then characterized through structural examination and hardness tests.

II. EXPERIMENTAL

The starting material for mechanical milling were powders of pure Ti of less than 150 μm in particle size

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and Y_2O_3 powder of ~ 40 nm in particle size. A mixture of powders of the composition of Ti-2 pct Y_2O_3 (percentage by weight) was milled in a SPEX 8000D high-energy shaker ball mill (SPEX SamplePrep, LLC, Metuchen, NJ) under a protective argon atmosphere. The ball-to-powder weight ratio was approximately 10:1. The milling process was carried out in 20-minute cycles with 10-minute breaks between the cycles. The total milling time was 20 hours. The cyclic milling was applied because in the case of a continuous process, the container would be heated too intensively. In the applied process, the temperature of the external wall of the container did not exceed approximately 313 K (40 °C). Powder sampling after different milling times was performed in a “glove-bag” purged with argon several times.

X-ray diffraction (XRD) of the powders after various milling times, heating in a calorimeter, and consolidation was carried out using a Rigaku MiniFlex II X-ray diffractometer (Rigaku Americas Corporation, The Woodlands, TX) with CuK_{α} radiation ($\lambda = 1.54178$ Å). The purpose of XRD was to examine the phase changes that took place during milling, heating in the calorimeter, and consolidation, as well as to determine the lattice parameter and estimate the mean crystallite sizes and mean lattice strain in the Ti matrix. To assess the mean crystallite sizes and mean lattice strain, the Williamson-Hall method was applied. For calculations from the XRD data, $CuK_{\alpha 1}$ radiation, after $K_{\alpha 2}$ stripping using the Rachinger method, was taken into account. The instrumental broadening was determined using a Si standard (provided with the diffractometer) and subtracted from the experimental breadth to obtain the “physical” broadening of each diffraction line, which was then used for the Williamson-Hall calculations.

The calorimetric examinations of the mechanical milling product were performed in a Perkin Elmer DSC-7 differential (Perkin Elmer, Inc., Waltham MA) scanning microcalorimeter. The tests were carried out in the temperature range of 323 K to 993 K (50 °C to 720 °C) with the heating rate of 40 K/min. During the measurements, the material remained under the atmosphere of spectrally pure argon. The calorimetric examinations were intended to determine the thermal stability of the product of the milling process.

Powder consolidation was carried out using a press with a high-pressure toroidal chamber. The chamber shape ensured quasi-isostatic pressing conditions. The hot pressing processes were conducted under the pressure of 7.7 GPa and temperature of 1273 K (1000 °C) for 180 seconds. The loading at the rate of 0.5 GPa/min was done prior to heating. The heating and cooling rate was 1000 K/min. Both the milling product and the initial mixture of powders (without milling) were consolidated.

Structural studies of the milled material after consolidation were performed in a JEOL 1200 EX transmission electron microscope (TEM; JEOL Ltd., Tokyo, Japan). The chemical composition of the bulk sample was examined using X-ray energy dispersive spectroscopy (EDS). Thin foils for the TEM observations were

prepared by cutting the material with a wire saw, dimpling, and finally thinning with Ar ion-beam milling.

Microhardness measurements were conducted by the Vickers method using a ZWICK microhardness testing machine (Zwick USA, Kennesaw, GA) under the load of 200 g (HV0.2) applied for 15 seconds. For each sample, 25 indentations were made.

III. RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction patterns of the powder mixture after selected milling times. In all the patterns, Ti and Y_2O_3 diffraction lines can be observed. However, one can observe that the Y_2O_3 peak intensity decreases with respect to that from Ti as the milling time increases. The reduction of Y_2O_3 peak intensity seems to be associated with the decrease in the Y_2O_3 particle size and increased lattice strains. A thorough XRD pattern analysis revealed a slight shift of the Ti diffraction lines toward the smaller angles with the increase of the process time. It is indicative of a slight increase in the Ti lattice constant values. Figure 2 illustrates the dependence of the Ti lattice constants on the milling times. As can be observed in the figure, the change in the lattice constants is very small; it was 0.36 pct for the c_0 parameter, whereas the a_0 parameter remained practically unchanged. It is, therefore, difficult to conclude

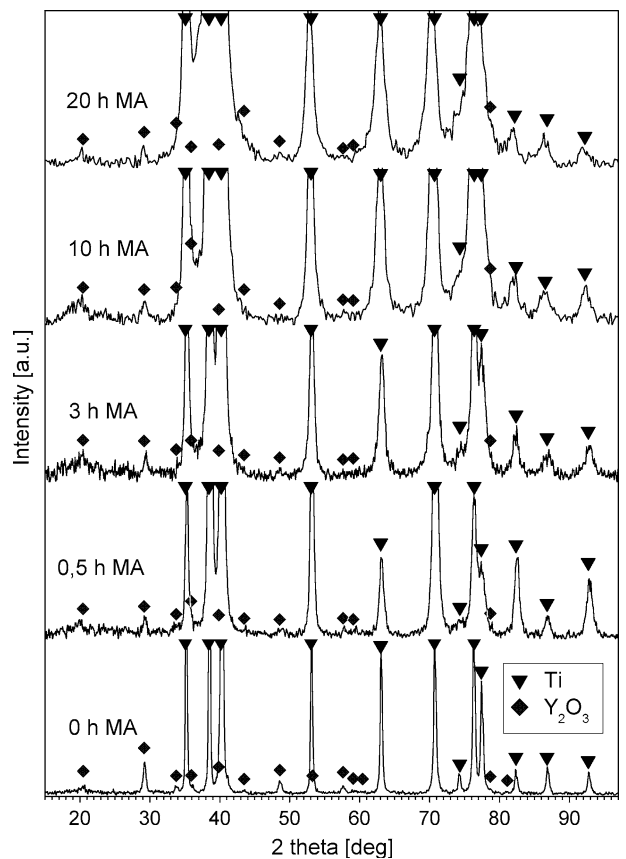


Fig. 1—XRD patterns of Ti and Y_2O_3 powders mixture after selected milling times.

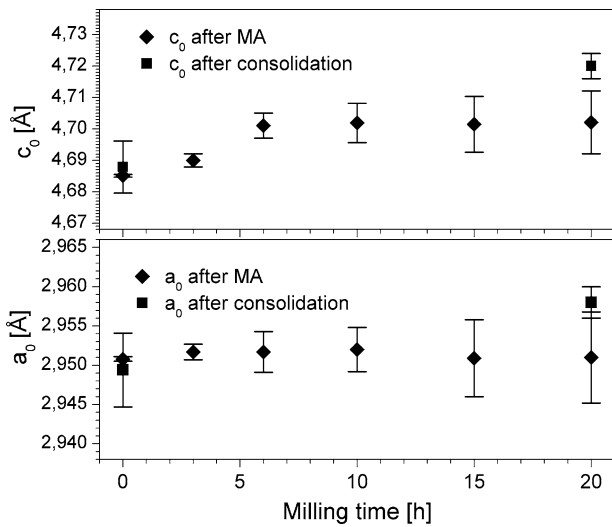


Fig. 2—Changes in Ti lattice constants in the milling time function and lattice constant values in the samples after consolidation.

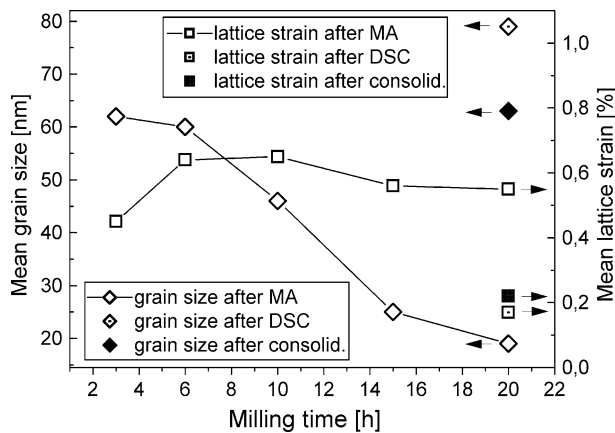


Fig. 3—Ti average crystallite size and mean lattice strain values after different mechanical milling times, after heating the milling product in a calorimeter, and after consolidation.

based on the above-presented results that Ti-based solid solution has been formed. It may be stated that a Ti matrix composite powder containing Y_2O_3 was synthesized as the final product of the performed mechanical milling process of the Ti and Y_2O_3 powders mixture.

The XRD patterns also reveal the widening of the diffraction lines from Ti as the process advances, which is caused by decreasing the average crystallite size and increasing the mean lattice strain. Changes in the estimated average crystallite size and in the mean lattice strain in Ti as a function of the milling time are presented in Figure 3. The Figure shows a significant decrease in the mean grain size between 6 and 15 hours of the process. The average crystallite size in the milling product (after 20 hours) is 19 nm; thus, the obtained composite powder has a nanocrystalline matrix. It can also be observed that the mean lattice strain was increasing until the 6th hour of the process, when it reached the steady-state value.

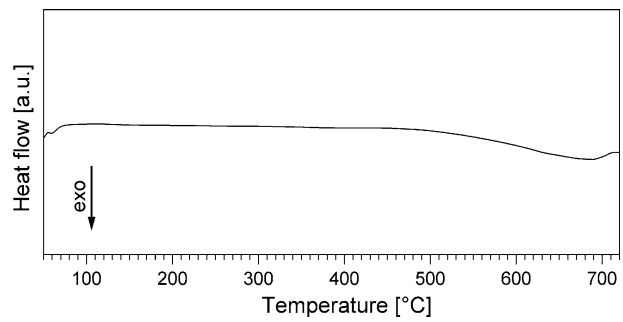


Fig. 4—Calorimetric curve recorded for the milling product.

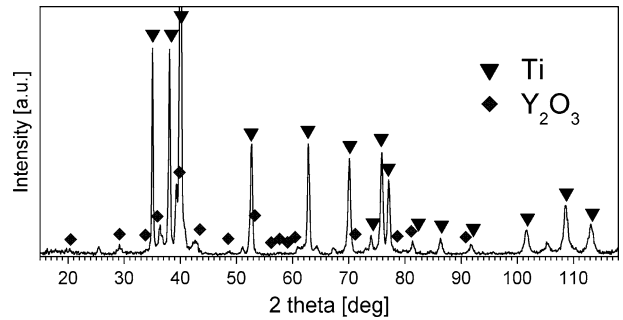


Fig. 5—XRD pattern of the milling product after heating up to 993 K (720 °C) in a calorimeter.

Figure 4 shows the calorimetric curve recorded for the final product of the milling process. The curve exhibits only a wide, low-intensity peak above the temperature of approximately 823 K (550 °C), connected with the exothermic effect. To test whether heating up to 993 K (720 °C) in the calorimeter caused any phase or structural changes, the sample after testing in a differential scanning calorimeter was investigated using the XRD method. The recorded XRD pattern is presented in Figure 5. The figure shows the presence of diffraction lines from Ti and Y_2O_3 in the pattern and reveals new lines of little intensity. It was not possible, however, to attribute the angular position of these lines to any phase containing Ti, Y, and O (Y_2TiO_5 , $YTiO_3$, or $Y_2Ti_2O_7$). Another detail visible in the XRD pattern of the powder after heating in the calorimeter is a decrease in the peak widths as compared with the pattern recorded after milling, which indicates an increase in the mean grain size and/or a decrease in lattice strain. The estimated values of the mean crystallite size and the mean lattice strain are 79 nm and 0.17 pct, respectively.

The initial (microcrystalline) powder and the powder after 20-hour mechanical milling were consolidated by hot pressing. The diffraction patterns of the bulk samples are presented in Figure 6 (also shown for comparison are the patterns of powders prior to consolidation). For both powders after consolidation, Ti diffraction lines can be observed, whereas Y_2O_3 peaks are not discernible from the background under the applied XRD scan conditions. Therefore, XRD examination was performed with higher resolution and increased intensity in the angular ranges corresponding

to the most intense Y_2O_3 diffraction lines in the standard pattern (25-1200 ICDD card): 100 pct (222), 46 pct (440), and 31 pct (622). The most intense diffraction peak of Ti (101) was also recorded under the same conditions. Figure 7 shows the results of these measurements (note that intensity is given in log scale). The examination revealed the presence of Y_2O_3 diffraction peaks. The XRD patterns of the solid samples (Figure 6) show additional lines of small intensity compared with those of the powder samples. The angular position of those lines could not, however, be attributed to any phase containing Ti, Y, and O (Y_2TiO_5 , $YTiO_3$, or $Y_2Ti_2O_7$). The comparison of the diffraction patterns of the mechanical milling product

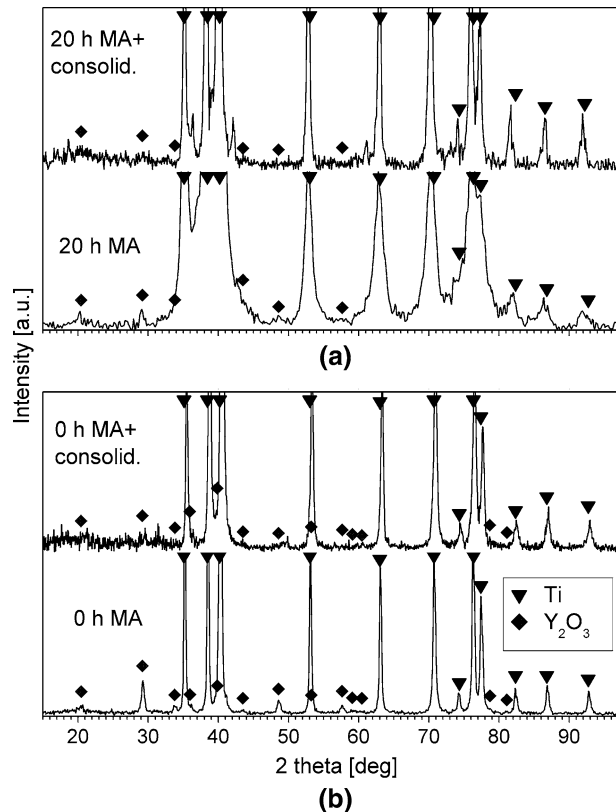


Fig. 6—XRD patterns of samples before and after consolidation: (a) powder after 20-h milling and (b) initial powder.

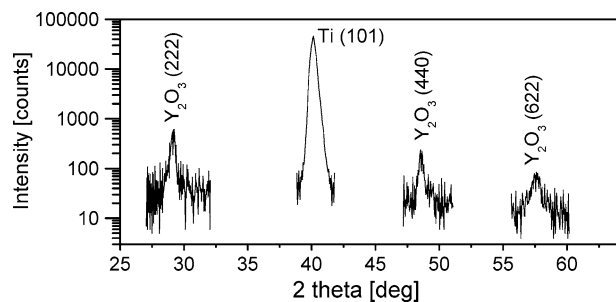


Fig. 7—XRD scans in the angular ranges corresponding to the most intense Y_2O_3 diffraction lines (222), (440), and (622), and to the Ti (101) diffraction peak recorded with higher resolution conditions.

before and after consolidation shows a decrease in the widths of the peaks from Ti, which indicates an increase in the mean grain size and/or a decrease in the mean lattice strain in the bulk material. The analysis of the XRD patterns allowed the authors to determine the lattice parameter values and to estimate the mean grain size and mean lattice strain for Ti in the consolidated samples (the Williamson-Hall method can be applied when the crystallite size is less than 100 nm; thus, the mean grain size or mean lattice strain were not assessed in the sample consolidated from the initial powders). The calculated values are presented in Tables I and II, and are illustrated in Figures 2 and 3.

The results obtained show that in the case of the initial powder mixture, the hot-pressing process did not cause any significant change in the Ti lattice parameter, whereas consolidation of the powder after milling led to an increase in the Ti lattice parameter. Furthermore, hot pressing of the powder after milling resulted in the increase in the mean grain size to 63 nm and a decrease in the Ti lattice strain. Thus, the applied consolidation parameters allowed preserving the nanocrystalline structure in the material. One should note that the mean grain size after heating in the calorimeter was 79 nm. Previous investigations showed that the application of high pressure influences grain growth at an elevated temperature by hindering it.^[19–21]

Studies of the material microstructure after milling and consolidation were performed in a TEM. Figure 8 presents the obtained images of microstructure. It can be observed that the grain size of the Ti matrix in the consolidated material varies widely from approximately 50 nm to approximately 200 nm. The dark-field images (Figures 8 (b) and (c)) reveal that some bigger grains are divided into subgrains. The presence of subgrains contributes to the observed widening of the diffraction lines in the XRD patterns. The values estimated with the Williamson-Hall method correspond to the mean value of the grain and subgrain size distribution in the material. Thus, the mean size of the Ti crystallites assessed with the XRD method and the grain size range observed in the TEM are consistent with each other. Furthermore, the TEM observations revealed the presence of small equiaxial particles of less than 30 nm in size, distributed uniformly in the Ti matrix. An analysis of the chemical composition, performed in TEM using the EDS method, showed the presence of Ti, Y, and O when areas including only small particles were analyzed, and of Ti exclusively when the matrix areas without particles were analyzed. This result, combined with the identification of the phase composition of the consolidated sample performed with the XRD method, shows that the small particles are Y_2O_3 . The recorded EDS spectra are presented in Figure 9.

The consolidated samples were also characterized by measuring their microhardness. Because of the small sizes of the samples after consolidation, the microhardness measurements were the only conducted tests on mechanical properties. The results obtained are included in Table II.

The microhardness of the nanocrystalline material (655 HV0.2) is high; it is 2.4 times higher than the

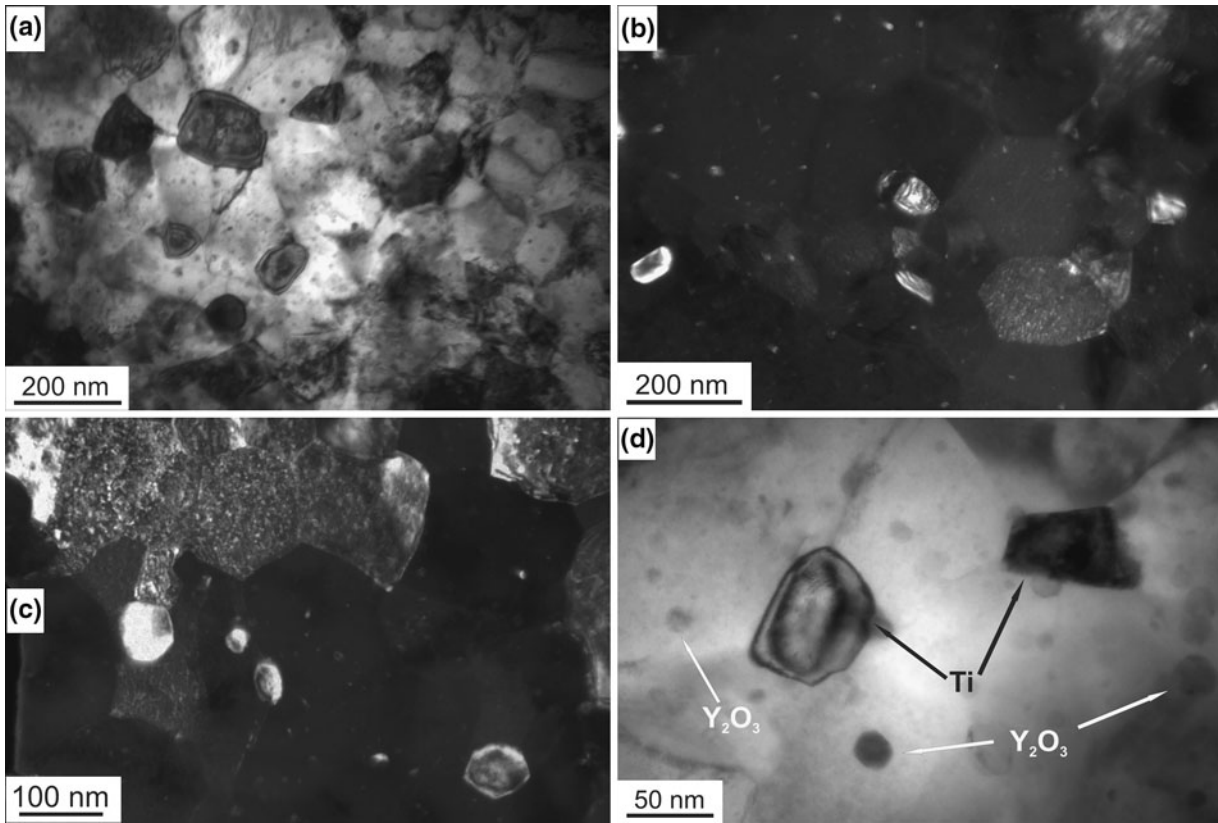


Fig. 8—TEM images of the consolidated milling product: (a) and (d), bright-field images, and (b) and (c), dark-field images obtained with the use of a fragment of Ti diffraction rings (100), (002), and (101).

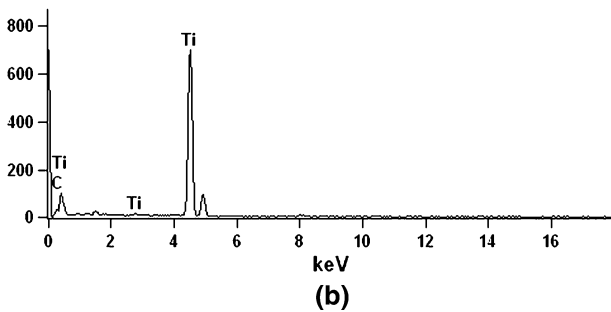
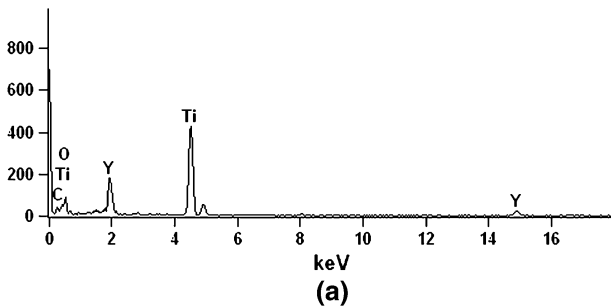


Fig. 9—EDS spectra: (a) from an area containing a small particle and (b) from the matrix grain area without particles.

microhardness of the consolidated initial powders mixture. Such high microhardness of the bulk sample obtained from the milled powder results from the reduction in grain size of Ti to the nanometer scale.

Another factor contributing to the high hardness is dispersion hardening. In the initial mixture, Y_2O_3 powder was merely mixed with Ti powder, whereas after the milling process, Y_2O_3 particles smaller than 30 nm were embedded within the Ti grains. The standard deviation of the nanocrystalline sample's microhardness value is small (4 pct), which proves that the material is uniform in the context of the tested property. The standard deviation of the microhardness value of the bulk sample obtained by the consolidation of the initial powder mixture is 10 pct.

IV. CONCLUSIONS

Mechanical milling of a Ti-2 pct Y_2O_3 powders mixture led to the synthesizing of a composite powder with a nanocrystalline Ti matrix. A significant decrease in the Ti mean grain size occurred between 6 and 15 hours of the process. After 20-hours of milling, the mean crystallite size in the milling product was 19 nm.

Both the nanocomposite powder prepared by milling and the initial mixture of powders were successfully consolidated by hot pressing under the pressure of 7.7 GPa at the temperature of 1273 K (1000 °C).

The consolidation process of the milling product resulted in a limited growth of Ti grains up to 63 nm and a reduction of mean lattice strain. The TEM investigations of the bulk sample revealed that Y_2O_3 equiaxial particles of less than 30 nm in size were distributed

Table I. Ti Lattice Parameter Values a_0 , c_0 in Powders after Different Milling Times and in Solid Samples

Milling time	Lattice Parameter of Ti in Powder		Lattice Parameter of Ti in Consolidated Material	
	a_0 (Å)	c_0 (Å)	a_0 (Å)	c_0 (Å)
0	2.9508 ± 0.0002	4.6851 ± 0.0004	2.9494 ± 0.0047	4.6879 ± 0.0083
3	2.9517 ± 0.001	4.6900 ± 0.0021		
6	2.9517 ± 0.0026	4.7011 ± 0.004		
10	2.9520 ± 0.0028	4.7019 ± 0.0063		
15	2.9509 ± 0.0049	4.7015 ± 0.0089		
20	2.9510 ± 0.0058	4.7021 ± 0.01	2.9580 ± 0.002	4.720 ± 0.004

Table II. The Mean Grain Size d , the Mean Lattice Strain η , of the Matrix and Microhardness HV0.2 Together with Standard Deviation (SD) Given in Percentage (SD_{pct}) for the Consolidated Material

Milling time	Powder		Consolidated Material		
	d (nm)	η (pct)	d (nm)	η (pct)	HV0.2 (SD _{pct})
0					273 (10 pct)
3	62	0.45			
6	60	0.64			
10	46	0.66			
15	25	0.56			
20	19	0.55	63	0.22	655 (4 pct)

uniformly in the nanocrystalline Ti matrix. Thus, the applied consolidation parameters made it possible to maintain the nanocrystalline structure of the material. Grain growth during consolidation at the increased temperature was most probably restricted by the application of high pressure.

The hardness of the produced nanocrystalline material is 655 HV0.2, and it exceeds the hardness of the microcrystalline material significantly (the consolidated initial mixture of powders), which confirms that reducing grain size to the nanometric level has a beneficial influence on the properties of titanium alloys. Dispersion hardening also contributes to the increase of hardness.

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