

## Studies on Nanostructured Titanium Silicide

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### Introduction:

Nanostructured materials have a significant fraction of the total atoms at their grain boundaries<sup>1</sup>, as their structure falls in between those of polycrystalline materials and amorphous materials. In polycrystalline materials most atoms are present within the grains and the grain boundaries consist of relatively few atoms. In contrast, amorphous materials do not have grains or boundaries. For this reason, the behavior of nanocrystalline materials is quite different from the behavior of conventional polycrystalline materials or amorphous materials. Of particular interest to mechanical engineers is the fact that nanostructured materials tend to have much greater hardness than conventional polycrystalline materials and also possess considerable high temperature ductility.

While the techniques for producing nanostructured materials as thin films have been relatively well established<sup>2</sup>, those for making bulky nanostructured products have received relatively little attention. Conventional sintering of a nanostructured powder would lead to significant grain coarsening and reversal to polycrystalline form. Attention therefore should be paid to the preservation of the nanostructure after consolidation into bulk. Some successful attempts have been made in this direction by employing self-propagating high temperature synthesis (SHS)<sup>3</sup> but there is need for investigating alternative routes for consolidation that ensure preservation of the nanostructure. The first author is the leader of several investigations looking into the possibility of employing the Equal Channel Angular Extrusion (ECAE) process for this purpose. It has already been demonstrated that nanostructured tungsten carbide billets can be successfully produced by subjecting mechanical alloyed (nanostructured) powder to ECAE<sup>4</sup>. In the present paper, the results of using this combination for producing titanium disilicide billets will be presented and discussed.

Silicides and silicide matrix composites involving titanium and molybdenum are considered as advanced high temperature materials. From the mechanical engineer's viewpoint, synthesis of nanostructured forms of these silicides would pave way for further improvement in the high temperature behavior as the hardness and the high temperature ductility of the nanostructured forms are much greater. With this in view, the present authors conducted an investigation involving the consolidation of nanostructured titanium disilicide powder. The powder was first mechanical alloyed (MA) to a fine size using an attritor, which is a high-energy ball mill. The fine powder was then consolidated using ECAE.

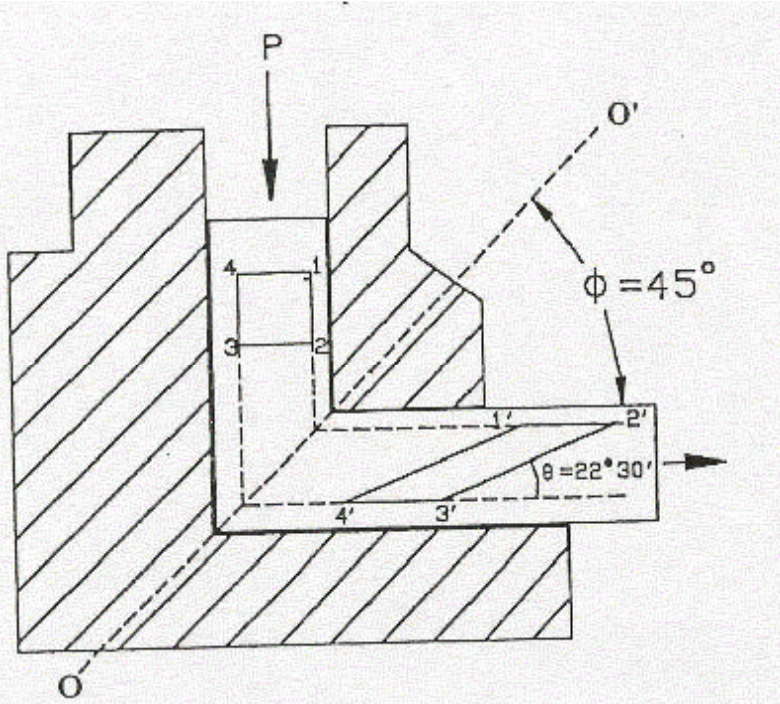
### Mechanical Alloying:

This process was originally developed by Benjamin<sup>5</sup> for producing oxide dispersion strengthened superalloys, but has since been used by many investigators to produce fine-scale powder. The attritor is popular equipment for mechanical alloying and consists of a vertical shaft with radial arms rotating in a chamber. The material to be milled is placed in the chamber along with the grinding balls made of hard materials. The milling is usually performed in an inert atmosphere.

The three important variables that control the quality of the powder being milled are, the milling time, the milling speed and the ball-to-powder ratio.

**Equal Channel Angular Extrusion Process:**

In this technique, severe plastic deformation is produced in the material being extruded, as a result of bulk shear<sup>6</sup>. Conventional polycrystalline material would be subjected to grain refinement in this method. As an extension, if nanostructured materials are being extruded, it is to be expected that such a structure would be preserved after extrusion by ECAE. This has been confirmed in the case of tungsten carbide by the first author and his associates<sup>4</sup>. Fig.1 shows a schematic illustration of the ECAE process.



**Fig.1 Schematic Illustration of ECAE Process**

**Experimental:**

Factorial design of experiments<sup>7</sup> is capable of providing information about the effects of variables and their interactions upon the properties of interest with relatively few experiments. Therefore this technique was employed to determine the effects of the three important attritor (MA) variables namely, the milling time, the milling speed and the ball-to-powder ratio, on the crystallite size of the milled (MA) powder and the microhardness of the powder compacts made by the ECAE process. The upper (+1) and the lower (-1) levels for the experimental design matrix were chosen as shown in Table-1. These were mainly based upon the operating limits of the attritor available with the authors.

Table-1: Levels of MA variables

Variable	Upper level (+1)	Lower level (-1)
Milling time (X <sub>1</sub> )	40 hr	10 hr
Milling speed (X <sub>2</sub> )	500 rpm	150 rpm
Ball-to-powder ratio (X <sub>3</sub> )	30:1	10:1

Based on  $2^3$  matrix, the powder batches were milled according to the combinations shown in the first three columns of Table-2. Each combination was repeated twice to assess the repeatability of the results. Commercial titanium disilicide (powder) was purchased in one lot and martensitic stainless steel balls of 3 mm diameter were used for grinding.

The milled powder was subjected to X-ray diffraction and the patterns were analyzed to determine the crystallite size using Scherrer's<sup>8</sup> formula. The principle of this method depends on the fact that there is broadening of X-ray diffraction peak as the crystallite size decreases and therefore the Bragg angle range at half-maximum height is a measure of the crystallite size. Each batch of powder was then placed in the cavity of a stainless steel container. The dimensions of the container were 25 mm square cross section and 250 mm length, with four cavities of 3 mm diameter drilled from the top to a depth of 75 mm. The four cavities were symmetrically located with respect to the center of the container section. Each cavity was purged with argon prior to filling with powder and covered with a stainless steel plug of 3 mm thickness. The plug was welded in place using ion beam welding. The stainless steel container was then annealed for 1 hr at 1200 C in argon atmosphere and extruded in the press of ECAE through  $90^0$ . After extrusion, the container was annealed again for 1 hr at 1200 C in argon and cooled to room temperature in the furnace. The consolidated titanium disilicide billets were then removed from the container using a slow speed diamond saw. The microhardness of each billet was then measured at several locations and averaged. Random samples of the billet were subjected to X-ray diffraction and it was found that there was no significant difference either in the crystallite size or the microhardness of the ECAE billets as compared to those of the milled powders. This indicates that the ECAE process is conducive to the preservation of the nanostructure with titanium disilicide, as in the case of tungsten carbide<sup>4</sup>. Fig. 2 shows a typical X-ray diffraction pattern obtained.

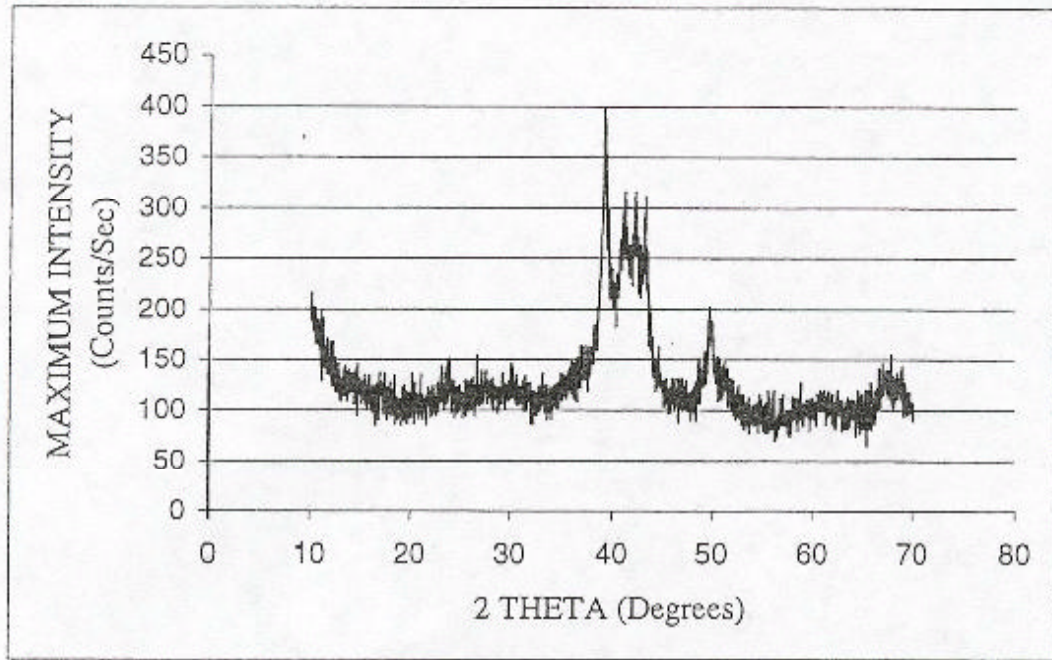


Fig. 2. Typical X-ray diffraction pattern of nanostructured titanium disilicide

### Results:

In Table-2 are shown the crystallite size and the microhardness of each of the eight combinations of the MA variables.

**Table-2: Test matrix and properties**

Milling time (X <sub>1</sub> )	Milling speed (X <sub>2</sub> )	Ball-to-powder ratio (X <sub>3</sub> )	Crystallite size (CS) nm	Microhardness (MH) VHN
+1	+1	+1	19	771
+1	-1	+1	40.5	809
+1	+1	-1	186	622
+1	-1	-1	66.5	753
-1	+1	+1	186	695
-1	-1	+1	74.5	691
-1	+1	-1	85	809
-1	-1	-1	66.5	674

The regression equations to be derived from the above table are of the form:

$$Y(X_1, X_2, X_3) = a_0 + a_1 X_1 + a_2 X_2 + a_3 X_3 + a_{12} X_1 X_2 + a_{23} X_2 X_3 + a_{31} X_3 X_1 + a_{123} X_1 X_2 X_3 \quad (1)$$

where,

$$a_0 = S(Y/N), a_1 = S(YX_1/N), a_2 = S(YX_2/N), a_3 = S(YX_3/N), a_{12} = S(YX_1 X_2/N),$$

$$a_{23} = S(YX_2 X_3/N), a_{31} = S(YX_3 X_1/N) \text{ and } a_{123} = S(YX_1 X_2 X_3/N).$$

Here, Y = crystallite size (CS) or microhardness (MH).

The nonlinear regression equation with interaction of coefficients was developed because it was found by standard statistical procedures<sup>9</sup> that the simpler linear equation was statistically inadequate. It was also confirmed while developing the nonlinear equations that the deviations of repeated results were within 5% of the mean and that the nonlinear equation was statistically adequate.

The regression equation obtained for the crystallite size was:

$$CS \text{ (nm)} = 90.5 - 12.5X_1 + 28.5X_2 - 10.5X_3 - 4X_1X_2 - 6X_2X_3 - 37.8X_3X_1 - 29.3X_1X_2X_3 \quad (2)$$

Likewise, the regression equation obtained for the microhardness was:

$$MH \text{ (VHN)} = 728 + 10.8X_1 - 3.8X_2 + 13.5X_3 - 38.5X_1X_2 - 4.8X_2X_3 + 37.8X_3X_1 + 28X_1X_2X_3 \quad (3)$$

### Discussion:

It is clear from equation (1) that higher milling time and higher ball-to-powder ratio have negative effects on the crystallite size, which is desirable. Higher milling speed by itself has a strong positive effect, which is undesirable. But the final crystallite size is decided not only by the individual effects but upon the interaction effects as well. For instance, higher values of all the three variables tend to reduce the crystallite size owing to the counteracting negative effect of the interactions on the positive effect of higher milling speed.

The microhardness of billets is affected positively by higher milling time and ball-to-powder ratio and somewhat negatively by higher milling speed. Also, higher values of all these three variables exert stronger positive effects than negative effects on the microhardness through their interactions.

### Recommended combination of the MA variables:

It is seen in Table-2 that the lowest crystallite size (19 nm) is obtained when all the three variables are at their higher values, but the best microhardness is obtained either with the higher milling time-lower milling speed-higher ball-to-powder combination, or with the lower milling time-higher milling speed-lower ball-to-powder ratio combinations. However, the crystallite sizes under these two combinations are significantly greater compared to the combination involving higher values of all the three variables. The microhardness under this latter combination is only about 4.7% lower than the microhardness in the first two combinations. It is therefore recommended that to get nanostructured titanium disilicide with fine crystallite size in the bulk form, mechanical alloying of the powder at higher milling time, milling speed and ball-to-powder ratio would be the best choice.

### Summary and Conclusions:

Statistical design of experiments was employed to determine the effects of three mechanical alloying (MA) variables namely, the milling time, the milling speed and the ball-to-powder ratio on the crystallite size and the microhardness of titanium disilicide. Equal Channel Angular Extrusion (ECAE) process was used for consolidating the MA powder. The results indicate that fine crystallite size and good microhardness obtained under the combination of higher milling time, higher milling speed and higher ball-to-powder ratio.

**A note on the educational value of this paper:**

This paper is the result of graduate research carried out by the second author under the supervision of the primary author. Two undergraduate students observed the research work at regular intervals and gained valuable information on nanostructured ceramics and their processing for the preservation of the fine-scale structure. The primary author teaches both senior-level undergraduate and graduate courses in materials science and plans to include the topic of this research in the updated versions of the courses.

**Bibliographic Information:**

1. G.E. Korth and R.L. Williams, "Dynamic consolidation of metastable nanocrystalline powders", Metallurgical and Materials Transactions, vol. 26A, 1995, p.2571
2. M. Greneche, "Interfaces, surfaces and grain boundaries in nanophase materials evidenced by Mossbauer spectroscopy, Materials Science Forum, vol. 307, 1999, pp.159-166
3. N.N. Mofa, T.A. Ketegenov and G.P. Metaska, "Self-propagating high temperature synthesis of ceramic material from mechanically activated materials", Chemical Physics Reports, vol. 16, 1997, pp. 903-910
4. M.N. Srinivasan, K. Ramakrishnan, X. Kaculi and K.T. Hartwig, "Microstructure and properties of mechanical alloyed and equal channel angular extruded tungsten carbide", Proceedings of the International Conference on Advanced Materials, Munich, Sept. 25, 2000.
5. J.S. Benjamin, "Fundamentals of mechanical alloying", Materials Science Forum, vol.90, 1992, p.1
6. H.J. Cui, R.E. Goforth and K.T. Hartwig, "The three dimensional simulation of flow pattern in equal channel angular extrusion", Journal of Metals, August 1998, p.23
7. W.G. Cochran and G.M. Cox, "Experimental Design", John Wiley, 2<sup>nd</sup> ed.,1950
8. P. Scherrer, Gottinger Nachr, vol.2, 1918, p.98
9. M.M. Shah, M.N. Srinivasan and M.R. Seshadri, "Assessment of bond and strength development in investment shells by design of experiments", Indian Foundry Journal, vol. 24, 1978, pp.10-15

**Biographic Information:**

Malur N. Srinivasan, Ph.D., P.E., is Professor and Chair of the Department of Mechanical Engineering of Lamar University in Beaumont, Texas. He has specialized in the area of Materials Processing and has over 110 publications in refereed journals and conferences. He has over thirty-five years experience in teaching mechanical engineering courses.

Venkataramanan Mandakolathur graduated from Lamar University, Beaumont, Texas with a Master of Engineering Science degree in mechanical engineering in 2000. He is presently employed by Trilogy Systems Corporation in Houston, Texas.

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