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Assessment of the Potential of Three Attritor-milled and Consolidated Nanostructured Materials for Sliding Wear-resistant Applications

Malur N Srinivasan*

This paper deals with the assessment of the potential of nanocrystalline tungsten carbide-cobalt (WC-Co), titanium disilicide ($TiSi_2$) and titanium silicide (Ti_5Si_3) for sliding wear-resistant applications. All the materials were milled in a laboratory attritor and the milled powders were consolidated using equal channel angular extrusion (ECAE) process in three cases and chemical consolidation using polycarbosilane (allylhydridopolycarbosilane-AHPCS) in one case. The microhardness of each consolidated sample was measured using a Vickers hardness tester. The crystallite sizes of WC-Co, Ti_5Si_3 and $TiSi_2$ consolidates after ECAE and Ti_5Si_3 after attritor milling and prior to chemical consolidation were determined using X-ray diffraction and, the relationship between the crystallite size and microhardness in these cases was examined. The data on microhardness of all the samples was analyzed with reference to current literature to assess the potential of each consolidate for sliding wear-resistant applications. The results indicate that attritor-milled Ti_5Si_3 consolidated using polycarbosilane as the binder appears to have the best potential for sliding wear-resistant applications. The experimental data reported in this paper was obtained by former graduate students under the direction of the author at Lamar University.

Keywords: *Tungsten carbide, Cobalt, Titanium disilicide, Titanium silicide, Attritor mill, Nanostructure, X-ray diffraction, Microhardness, Sliding wear.*

1.0 INTRODUCTION

Nanocrystalline materials have grain size of about 1000 nm or lower and have a large fraction of their atoms residing in the grain-boundary region, as opposed to conventional polycrystalline materials where only a small fraction of atoms are present, as discussed by Siegel and Thomas [1]. As a result, these materials exhibit properties quite different fro those of conventional polycrystalline and amorphous materials. As discussed by Koch [2] bulk properties may be dramatically changed in nanocrystalline materials as compared to polycrystalline materials of the same composition. In particular, the hardness can increase up to 7 times when the grain size is changed from above 1000 nm to about 10 nm. However, as discussed by Carlton and Ferreira [3] the hardness may decrease significantly when the grain size is reduced below about 10 nm, being governed by inverse Hall-Petch relationship. Hardness is an important factor governing the wear resistance of a material and as a first approximation, it may be expected that materials with a grain size in the nano-range (10-1000nm) would possess superior wear resistance in relation to their conventional polycrystalline counterparts; this postulation has indeed been confirmed by Jia and Fischer [4] for sliding wear of WC-Co.

*Department of Mechanical Engineering Lamar University Beaumont, Texas - 77710, USA. E-mail : malur.srinivasan@lamar.edu

In sliding wear it is customary to determine the volume of the material removed which may be expressed as

$$V = kPs/H \quad ....(1)$$

where, V is the volume removed (m^3), P is the load (N), s is sliding distance (m), H is the hardness (N/m^2) and k is the wear coefficient (dimensionless). Rearranging the terms in equation (1) gives

$$V/Ps = k/H \quad ....(2)$$

which is termed the wear rate and it is seen that it has an inverse relationship with the hardness. In the results obtained by Jia and Fischer [4] for tungsten-cobalt alloy of various grain sizes, this is indeed the trend. In the same paper it is also seen that the wear coefficient decreases with the increase in grain size only when the grain size is greater than about 0.5 μm. In their samples that had about 70 nm size, the wear coefficient is significantly lower than what is predicted by extrapolating from 500 nm to 70 nm grain sizes. In this paper, the wear rate vs. hardness shows higher values than what could be predicted by linearly extrapolating the values from 500 nm and above grain size samples, evidently due to reduction in k values.

The final conclusion by Jia and Fischer [4] is that nanostructured WC-Co consolidates, which have higher hardness, have greater sliding wear resistance than their conventional micrograined counterparts and this provided the present author with the impetus to assess the potential of three attritor-milled nanostructured materials compacted using equal channel extrusion (ECAE) process and one attritor-milled material compacted using polycarbosilane for sliding wear resistant applications.

2.0 EXPERIMENTAL

2.1 Attritor milling in all the cases was done based on 2^3 factorial design of experiments detailed in Montgomery's book [5]. The three variables considered were milling time, milling speed and ball-to-powder ratio. The powders used were tungsten, graphite and cobalt (6 wt. %) for WC-Co alloy, Ti_5Si_3 and $TiSi_2$ in the attritor, for the three materials investigated. All were in powder form, had 99.5% purity and a mesh size of 325. The high levels for milling time, milling speed and ball-to-powder ratio were 40 hr, 500 rpm and 30:1 respectively. The corresponding low levels were 10 hr, 150 rpm and 10:1 respectively. Eight experiments were performed as detailed by Montgomery [5], with two replications in each case. The milled powder with the balls in each case was carefully emptied from the attritor chamber into separate containers in a controlled-atmosphere glove box. After carefully separating from the balls, each batch of the milled powder was stored there until consolidation. A schematic illustration of the attritor similar to the one used is shown in Figure 1.

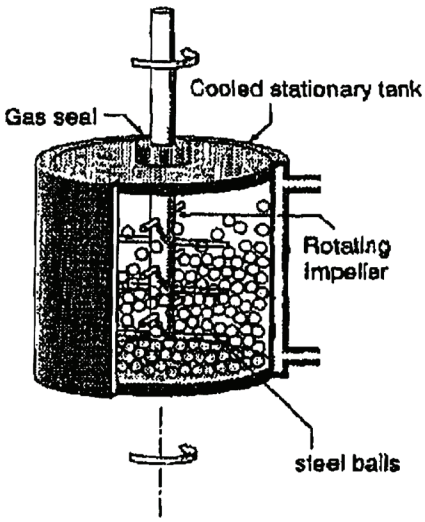

FIG. 1 SCHEMATIC ILLUSTRATION OF AN ATTRITOR [6]

2.2 ECAE Consolidation

Milled powder of tungsten carbide-6 wt.% cobalt prepared by Ramakrishnan [7], titanium silicide (Ti5Si3) prepared by Kaculi [8], titanium disilicide prepared by Mandakolathur [9] were consolidated using equal channel angular extrusion (ECAE) available at Texas A&M University at College Station, Texas, as described in the references cited above. Figure 2 shows a schematic illustration of the ECAE process.

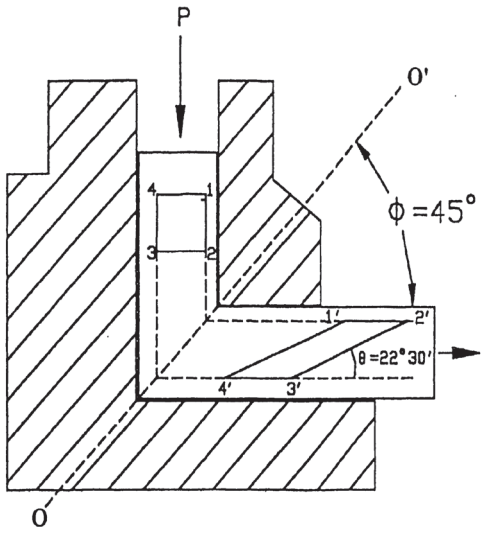

FIG. 2 SCHEMATIC ILLUSTRATION OF ECAE PROCESS [7]

Figure 2 shows a 0.025 m square stainless steel bar subjected to ECAE. The milled powder was placed in four symmetric holes of 0.003 m diameter drilled in the bar. The holes were then sealed at the top by using ion beam welding at Ames DOE Laboratory at Ames, Iowa. After annealing the sealed billet at 1200^{0}C for 1 hr in argon, it was extruded using the ECAE facility at Texas A&M University. Route A, in which the same orientation is maintained between the shear plane and the shear direction with respect to the extrusion direction (Figure 2) was used. This route is meant to better compaction as discussed by Parasiris [10]. The four billets of consolidated material were then extracted from each stainless bar and annealed again in argon for 1 hr at 1400^{0}C for testing and analysis. Two items of interest in all these investigations are the crystallite size and the microhardness of each batch. The latter was determined using a Buehler Micronet II digital microhardness tester with a diamond pyramid indenter, as per ASTM E-384 [11]. For crystallite size determination, the billets of the consolidates were ground using a hammer mill and loaded into a plastic holder. X-ray diffraction pattern each batch was then obtained using a Seifert-Scintag PAD-V diffractometer using Cu-K-alpha radiation. In Figure 3 is shown a typical diffraction pattern obtained by Ramakrishnan [7]. The crystallite size was obtained from the diffraction pattern using Scherrer's equation, cited by Bartram[12].

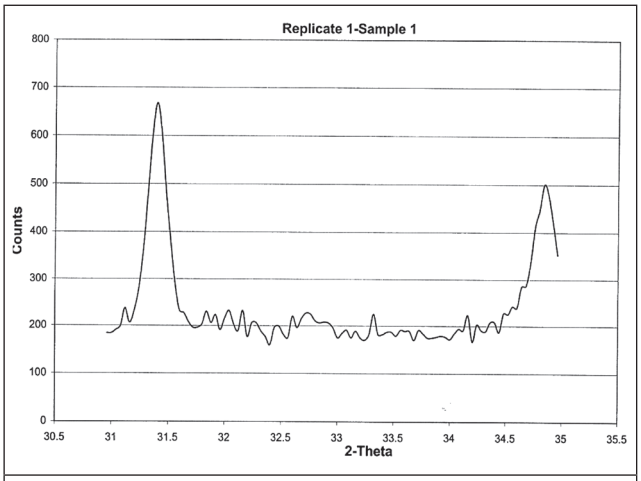

FIG. 3 TYPICAL X-RAY DIFFRACTION PATTERN FOR WC-CO [7]

2.3 Chemical Consolidation

Aripaka [13] used polycarbosilane (Allyl Hydrido Polycarbosilane-AHPCS) at 7.5 wt.% of the attritor-milled powder for consolidating chemically rather than extruding using ECAE. The powder and the binder (AHPCS) were mixed thoroughly in dough mixer for 2 hr and cured at 200^{0}C to attain sufficient green strength after compaction. The microhardness of each green compact was determined as explained earlier and the compacts were fired in a controlled atmosphere furnace at 1400^{0}C. The microhardness of each compact was measured again after firing. The crystallite size of each batch was measured as before and was correlated with the microhardness of the low

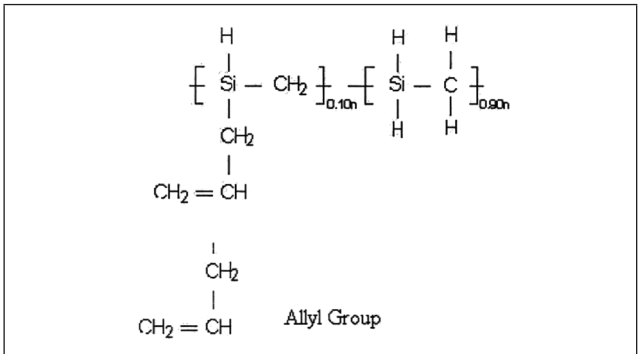

FIG. 4 STRUCTURAL FORMULA OF AHPCS

temperature cured compacts as it was feared that significant grain growth would occur after firing at 1400° C. This turned out to be an unnecessary fear as the crystallite size in a representative sample of

the material (Ti_5Si_3) after firing was found to be only around 50 nm, being well within the nano-range. Interpretations on potential for sliding wear resistance of these samples were based on the microhardness after firing, but sufficient data was not available to determine the crystallite size vs. hardness relationship after final consolidation unlike in ECAE-consolidated samples. In Figure 4 is shown the structural formula for AHPCS.

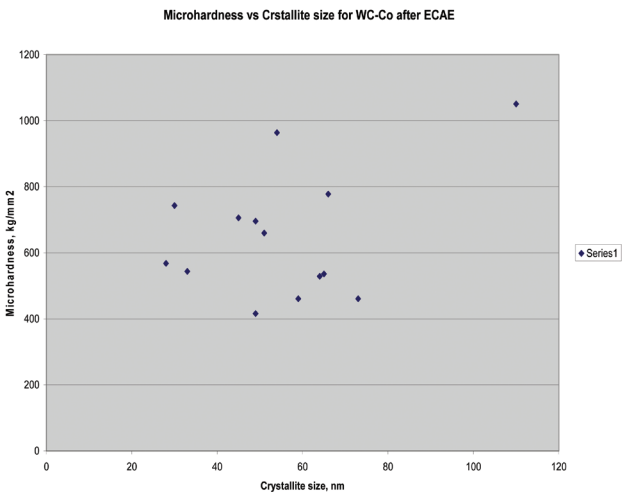

FIG. 5 MICROHARDNESS VS. CRYSTALLITE SIZE FOR WC-CO AFTER ECAE [7]

3.0 RESULTS AND DISCUSSION

3.1 WC-Co milled in attritor and consolidated using ECAE

In Figure 5 is shown the variation of microhardness with crystallite size for WC-Co as obtained by Ramakrishnan [7]. The data or both replicates have been included to better show the trend. The maximum microhardness is about 1050 kg/mm^2 which is far less than the microhardness of over 2000 kg/mm^2 obtained by Jia and Fischer [4] for nanostructured samples. However, the crystallite size is in the range of 28 nm to 110 nm, as compared to 70 nm reported by the above authors. Thus it is clear that the ECAE consolidation gives fine grains but lower microhardness as compared to pressed and sintered WC-Co samples studied by Jia and Fischer [4]. To understand why a sample that had a crystallite size of 59 nm showed microhardness of only about 460 kg/mm^2, an SEM examination of this sample was made. The SEM picture is shown in Figure 6.

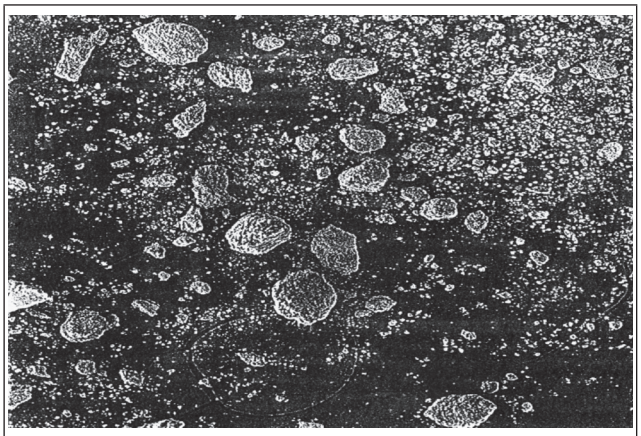

FIG. 6 SEM PICTURE OF SAMPLE WITH CRYSTALLITE SIZE OF 59 NM AND MICROHARDNESS OF 461 KG/MM^2 , X100 [7]

It may be seen that there is some local aggregation of carbide and large islands of cobalt, with nano-grains of carbide segregated in the top corner. This heterogeneous nanostructure is evidently due to heavy shear to which the sample is subjected in ECAE. Thus it is clear that the WC-Co samples processed by Ramakrishnan [7] preserve nanostructure in the consolidates, which is rather difficult to achieve in pressed and sintered samples due to excessive grain growth [4]. However they generally have unacceptably low microhardness and therefore may be considered unsuitable for sliding wear-resistant applications. One way of mitigating this problem is to try to alloy WC-Co with vanadium carbide [4], or use the present ECAE consolidate as nanostructured feed stock for laser surface hardening. The consolidate would be safer and easier to handle as compared to unconsolidated attritor-milled powder.

3.2 Ti_5Si_3 milled in attritor and consolidated using ECAE

In Figure 7 is shown the variation of microhardness with crystallite size for Ti_5Si_3 as obtained by Kaculi [8]

It is seen from Figure 7 the crystallite size of Ti_5Si_3 is in a narrow range of 1.79 nm to 2.21 nm

and the microhardness is in the range of 337 kg/mm^2 to 705 kg/mm^2. The microhardness roughly follows the inverse Hall-Petch relationship, which is to be expected as the grain sizes are all well below 10 nm. This trend, coupled with the fact that the maximum hardness is only about 700 kg/mm^2 again rules out this consolidate for any consideration of sliding wear-resistant applications. The mitigating considerations would be to make of a composite of TiC or TiN and $Ti_5Si_3$with selective laser melting [14-15] using ECAE consolidated Ti_5Si_3 as nanostructured feed stock for laser surface hardening.

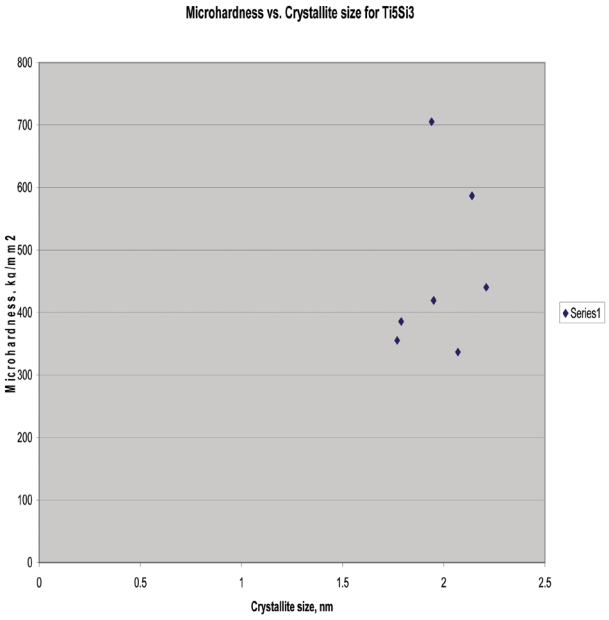

FIG. 7 MICROHARDNESS VS. CRYSTALLITE SIZE FOR TI_5SI_3 AFTER ECAE [8]

3.3 $TiSi_2$ milled in an attritor and consolidated using ECAE [9].

In Figure 8 is shown the variation of microhardness with crystallite size in attritor-milled and ECAE-consolidated $TiSi_2$ as obtained by Mandakolathur [9].

It is seen that Hall-Petch relationship is roughly observed and the nanostructure is coarser than in $Ti_5 Si_3$. However, the microhardness values are not high enough for wear-resistant applications. The mitigating factors considered for ECAE consolidated $Ti_5 Si_3$ may be applicable here as well.

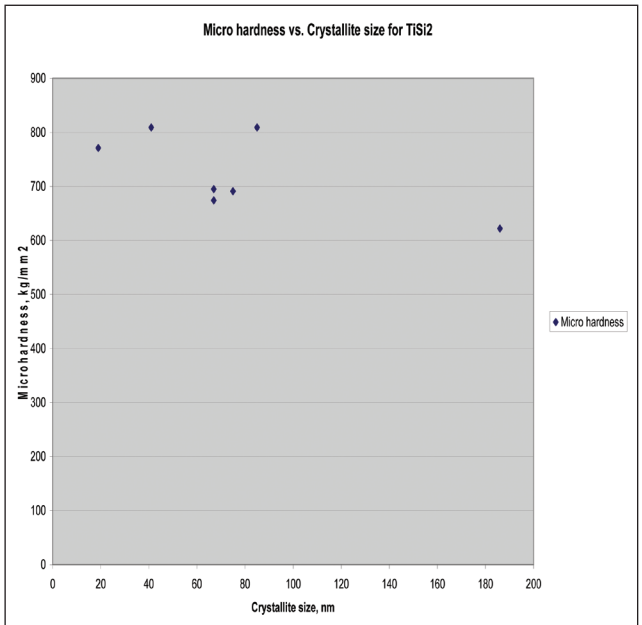

FIG. 8 MICROHARDNESS VS. CRYSTALLITE SIZE FOR $TISI_2$ AFTER ATTRITOR MILLING AND ECAE CONSOLIDATION

3.4 Ti_5Si_3 milled in an attritor and consolidated using a chemical binder, AHPCS.

Unlike the previous cases, the consolidates were fired at 1400^{0}C and therefore some grain growth occurred after attritor milling. When the grain size was measured after firing in a representative case to ensure that the nanostructure was retained even after firing, the crystallite size increased from 16.43 nm to 52 nm after firing at 1400^{0}C, which is well within the nano-range. The crystallite sizes after attritor milling were determined using X-ray diffraction of milled powder and are shown in Table 1 along with microhardness obtained after mixing the milled powder with AHPCS, after curing and then firing.

The microhardness after curing (to attain green strength) is roughly indicative of the effect of attritor milling as the binder is fully effective only after firing. It is thus seen that unlike in ECAE-consolidates, the microhardness in AHCPS-consolidates can be as high as 1134 kg/mm^2 after firing, the crystallite size remaining in the nano-range even after firing. The attritor-milled powder was subjected to mild pressure in a specimen mounting press prior to curing and firing. Had suitably high pressure been used to compact the

attritor-milled powder prior to curing and firing, the results may have been good enough to qualify for consideration of wear-resistant applications. It may be mentioned in this context that Sabooni, Karinzadeh and Abbasi [16] have that the fracture toughness of $Ti_5 Si_3$ could be significantly improved in the nanostructural form. By analogy with WC-Co [4] it may thus be possible to improve the sliding wear resistance as well.

TABLE 1
CRYSTALLITE SIZES AND MICROHARDNESS OF TI_5SI_3 ATTRITOR MILLED AND CONSOLIDATED WITH AHCPS AS THE BINDER

Experiment number	Milling Speed, rpm	Ball-to-powder ratio	Milling time, hr	Crystallite size, nm	Microhardness after curing at 200^0C, kg/mm^2	Microhardness after firing at 1400^0C, kg/mm^2
1	150	10	10	1.65	297.2	754.2
2	500	10	10	2.5	387.3	893.7
3	150	30	10	16.43	387.9	940.5
4	150	10	40	11.74	329.7	1133.9
5	500	30	10	16.73	276.2	706
6	500	10	40	9.45	419.8	1106.9
7	150	30	40	9.4	336.6	916.3
8	500	30	40	9.55	354.9	961.2

4.0 SUMMARY

It is thus observed that attritor milling and ECAE consolidation is good for preserving the nanostructure in the three materials studied, but the consolidates are unsuitable for sliding wear- resistant applications in the as-processed billet form. If one has to persist with the ECAE process for eventual production of sliding wear-resistant nanostructured billets in the materials studied, other routes for ECAE as well as material modifications will have to be examined. On the other hand, attritor milling and chemical consolidation with AHPCS appears to have the best potential for sliding wear-resistant applications of Ti_5Si_3 provided suitably high pressure is used along with chemical consolidation.

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