EFFECT OF HIGH ENERGY MILLING PARAMETERS ON NANOSTRUCTURED Cr_3C_2-Ni20Cr POWDER CHARACTERISTICS.

C.A.Cunha[1a], A.G.F.Padial[1b], N.B.de Lima[1c], J.R.Martinelli[1d], O.V.Correa[1e] and L.V.Ramanathan[1f]

[1] Centro de Ciência e Tecnologia de Materiais,
Instituto de Pesquisas Energéticas e Nucleares (IPEN-CNEN-SP),
Av. Prof. Lineu Prestes 2242, Cidade Universitária,
05508-000 São Paulo. SP
[1a] cacunha@ipen.br@ipen.br , [1f]lalgudi@ipen.br

Abstract

Cr_3C_2-NiCr coatings have been used for corrosion and wear resistant applications. In the last decade, thermal sprayed coatings using nanostructured feed stock of other materials has exhibited higher hardness, strength and corrosion resistance. Hence, it is anticipated that nanostructured Cr_3C_2-NiCr coatings will also exhibit these properties and therefore posses improved performance characteristics. Preparation of nanostructured feed stock powders is the first step in the synthesis of nanostructured coatings and mechanical milling is an effective process to obtain the powders. Preliminary studies in which commercial Cr_3C_2-NiCr powders were milled in hexane and gaseous nitrogen revealed that particle and crystallite size were significantly smaller in powders milled in nitrogen. This paper presents the effect of hexane content and milling parameters on Cr_3C_2-Ni20Cr powder characteristics. Use of just sufficient hexane as the milling media reduced significantly the particle and crystallite sizes.

1. Introduction

Since the pioneering work of Benjamin et al. (1) in the late 1960s and early 1970s, the process widely known as “Mechanical Alloying” (MA) has evolved considerably. Originally its use was intended to produce dispersion-strengthened Ni base superalloys. This process enabled the production of homogeneous composite microstructures in the sub-micrometer scale, and the mechanism by which this was achieved was attributed to repeated deformation, welding and fracture of powder particles in the high-energy mill (1 - 4). In the 1980s and 1990s, a number of studies involving a wide variety of powder systems were carried out and this established MA as a robust powder processing route(4). In MA, extensive cold work produces a very high degree of microstructure refinement and this resulted in nanocrystalline structures, or non-equilibrium structures (4 - 6).
Nanocrystalline materials generally have grain sizes lower than 200 nm(5) and the improved physical and mechanical properties of the materials are due to the nanometer scale grain size as well as high volume fraction of grain and interface boundaries (5 - 7). Nevertheless, maintenance of the fine microstructure at high temperatures is still a challenge and many investigations are on-going to address this issue, especially the use of cryogenic milling media to produce structures with enhanced thermal stability.
Recently the effect of milling media on the characteristics of high energy milled nanostructured Cr_3C_2-Ni20Cr powder was evaluated (5 - 7). Gaseous nitrogen and hexane were used as the milling media and the particle as well as crystallite sizes of Cr_3C_2-Ni20Cr powders milled in nitrogen were significantly smaller compared with that milled in hexane. Nevertheless, significant reductions in

particle and crystallite size of these powders milled in hexane compared to that in gaseous nitrogen have been reported[7].
This paper presents the effect of hexane content on high energy milled Cr_3C_2-Ni20Cr powder characteristics.

2. Materials and Methods

In this study, a ZOZ high energy mill operating at 400 rpm and with a ball to powder ratio of 10:1 was used to mill Cr_3C_2-Ni20Cr powder for 8 hours. Hexane was used as the milling media and 2 batches of milled Cr_3C_2-Ni20Cr powders were prepared with 100g of powder/ 50ml of hexane and 100g of powder/10ml of hexane, respectively. The particle size, morphology, grain size and phase constituents of the milled powders from the different batches were determined and compared with the "as received" powder. A CILAS particle size analyzer was used to determine the average particle size and a scanning electron microscope (SEM) coupled to an energy dispersive system (EDS) was used to determine particle morphology and the composition of the phases. The composition of the 'as received' and the milled Cr_3C_2-Ni20Cr powders was determined by x-ray fluorescence analysis. X-ray diffraction (XRD) analysis was used to determine the crystallite size of the powders. The Scherrer equation (1) was used to determine the crystallite size[8]. This equation relates crystallite size (D) and the full-width at half-maximum (FWHM), referred to as Δ (2θ) of XRD reflections.

$$D = 0,9\, \lambda / \Delta (2\theta) \cos\theta \qquad (1)$$

Where λ is the wavelength (in the case of Cu target, λ= 0,15406) and θ is the diffraction angle. The use of this equation is based on the physical origin of broadening of the XRD reflections by the small grain size only. True peak broadening Δ (2θ) can be obtained using equation (2):

$$\Delta (2\theta) = [(\Delta (2\theta)_h)^2 - (\Delta (2\theta)_g)^2]^{1/2} \qquad (2)$$

Where $\Delta(2\theta)_h$ is the FWHM of the measured profile and $\Delta(2\theta)_g$ is the FWHM of the profile from the standard sample for the same reflection. The grain size thus obtained is volume averaged in the direction perpendicular to the diffraction plane.

3. Results and Discussion

Table 1 shows the chemical composition of the as-received and the milled powders. Marked increase in the iron and oxygen content with decrease in hexane content can be observed. This is considered to be due mainly to removal of the iron oxide from the surface of the balls and the wall of the milling container.

Table 1: Chemical Composition (weight %).

	Cr	**Ni**	**W**	**Fe**	**Co**	**O**
AR (*)	79.345	16.011	2.777	0.304	0.325	0.134
100g/50ml	75.698	19.359	2.416	1.378	0.365	0.599
100g/10ml	75.231	18.547	2.519	2.876	0.267	0.680

(*) As received.

The average particle sizes of the Cr_3C_2-25%Ni20Cr powders milled for 8 hours with different amounts of hexane, as well as the "as received" powder, are shown in fig. 1. A significant decrease in particle size of the milled powder, compared to the as-received powder is evident. The particle size decreased also with reduction in the amount of hexane used as the media. For comparison, the average particle size obtained under similar conditions by Ramanathan et al.[7] was around 14,5 μm and is shown in fig.1. In this investigation the powder lots contained 50% and 10% of the amount of hexane used in the above mentioned reference. The decrease in particle size with reduction in the amount of hexane used as the milling media can be attributed to the cushioning effect that hexane exercises during the milling process. The impact energy transferred to the powder particle is lower when the amount of hexane is higher indicating that hexane coated all surfaces, reducing thereby the impact energy transfer during particle-particle, particle-ball or particle-container wall contact.

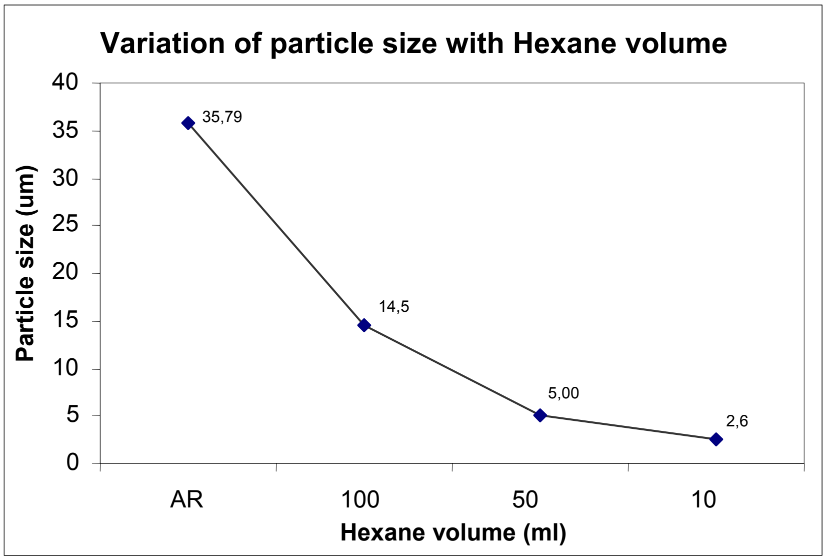


Fig. 1. Particle size of powders milled for 8 hours, as a function of the hexane volume (ml). Notice that AR indicates "as received" and 100ml was the hexane volume used in reference (7).

The x-ray diffraction patterns of the milled powders revealed peaks corresponding to Cr_3C_2 and the binder, Ni20Cr alloy. A typical diffraction pattern is shown in fig.2. These peaks were considered and equation (1) was used to determine crystallite sizes. The average crystallite size of the Cr_3C_2 particles, as well as that of the Ni20Cr alloy, in the milled powders decreased significantly with reduction in the amount of hexane added, as shown in fig.3. The crystallite size of the powder milled with 100ml of hexane was reported to be around 100 nm.[7] This reduction in crystallite size with decrease in hexane content can be also related to increase in the impact energy during milling.

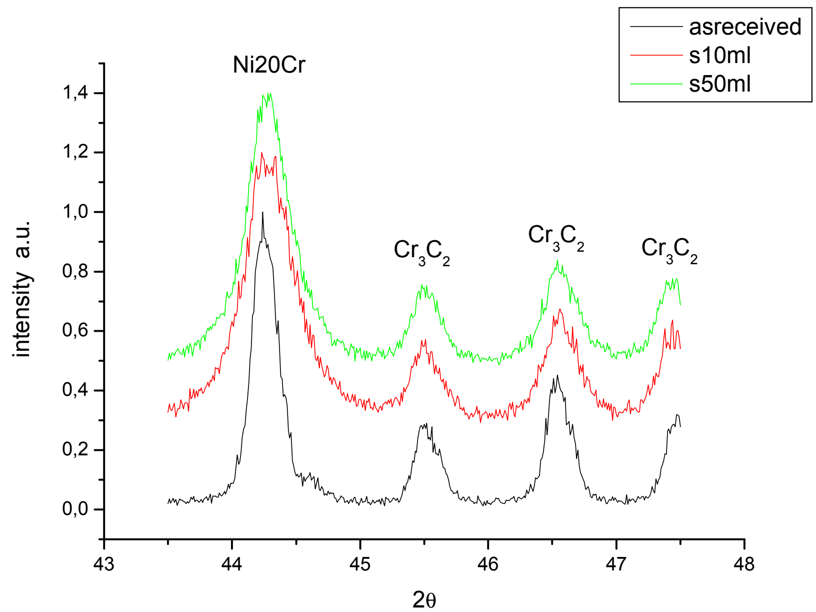


Fig. 2. X-ray diffraction patterns of the powders: AR ("as received") and 50ml and 10ml of hexane are of powders milled for 8 hours.

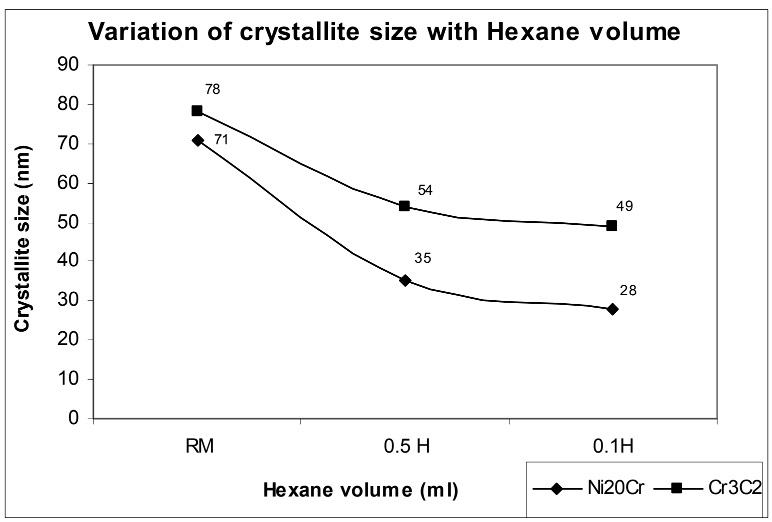


Fig. 3. Crystallite sizes of powders milled for 8 hours, as a function of hexane volume (ml).

The as-received and milled powders were examined in the SEM. As is usual of powders prepared by high energy milling, the hard Cr_3C_2 particles are embedded in the ductile Ni-Cr alloy phase. Similar observations were reported earlier(7). The micrographs also revealed metal(alloy)-ceramic composites that formed during the milling process.

Marked changes in particle morphology and size of high energy milled powders can be observed upon comparing micrographs in figs. 4 and 5. The as-received powders are spherical and homogeneous. The milled powders are smaller and are no longer spherical. The powder milled with 10ml of hexane is significantly finer than that milled with 50ml of hexane. The micrographs in Figs. 5 (b) and (d) also reveal faceted Cr_3C_2 particles and some with embedded Cr_3C_2 particles in the ductile Ni-Cr alloy phase.

The energy dispersive spectra of the "as received" (AR) and 50ml of hexane and 10 ml of hexane milled powders were similar and are shown in Fig. 6. In-situ analyses of several particles were carried out and the composition of the as-received powders indicated 79.96 at% Cr and 20.04% Ni.

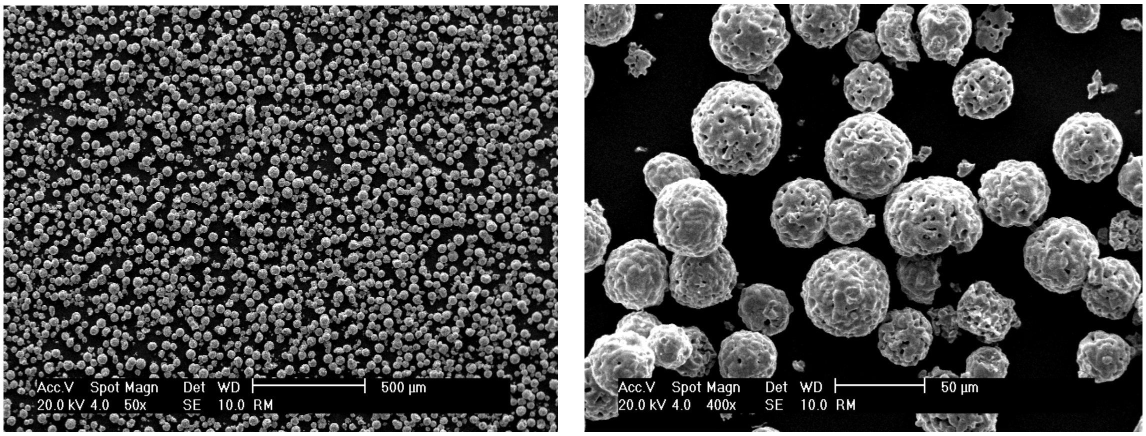
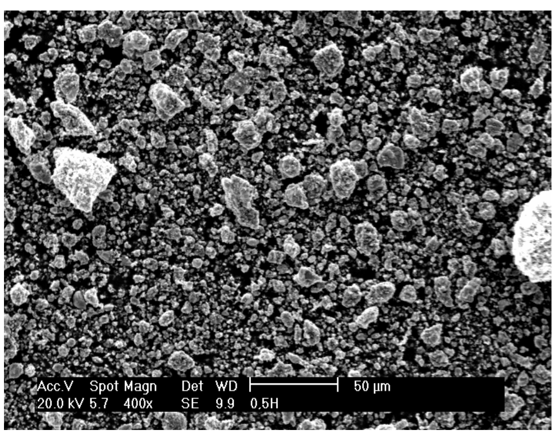
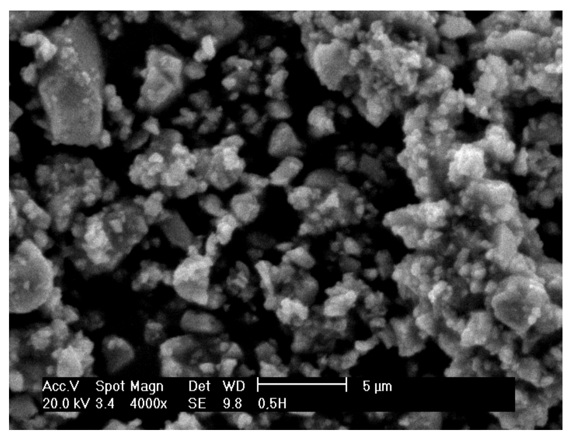


Fig. 4. Secondary electrons images at different magnifications of the powder in the "as received" (RM) condition.

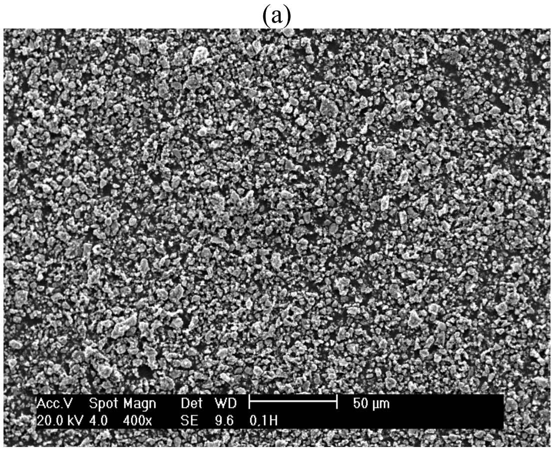
Similar analysis of powder milled with 50ml of hexane revealed a small increase in the Cr content of the ductile phase (Cr = 83.60 at % and Ni = 16.40 at %), and this could be attributed to the milling process itself. Analysis a Cr_3C_2 particle embedded in the ductile Ni-Cr alloy phase is shown in Fig.6 (c) and it revealed 95.95 at % Cr and 4.05 at % Ni.



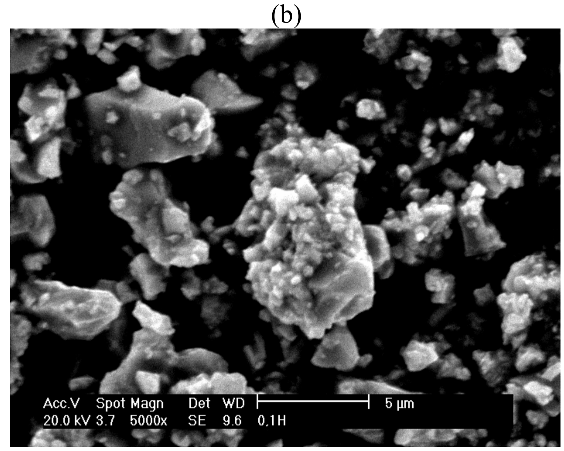
(a)



(b)

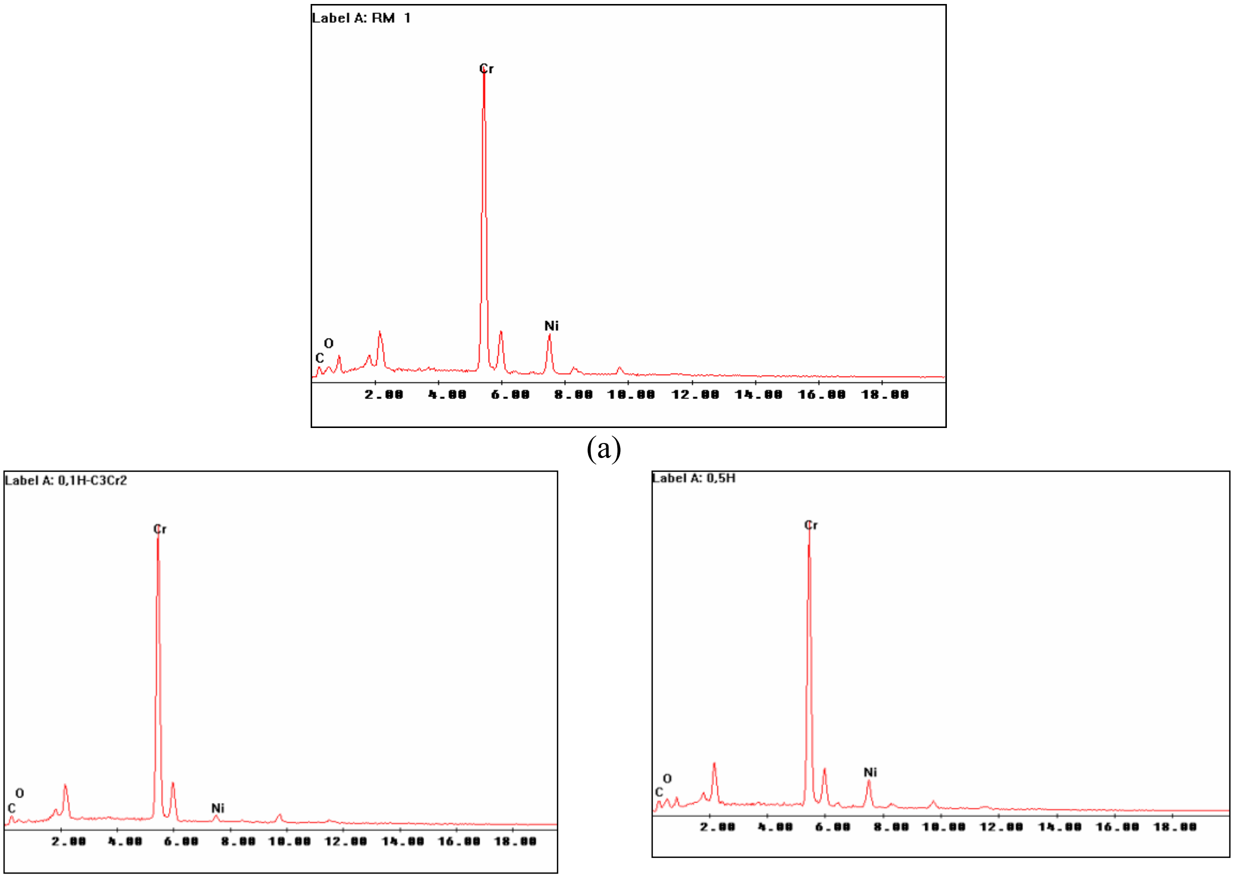


(c)



(d)

Fig. 5. Secondary electrons image of the powders milled for 8 hours: (a) and (b) 50ml of hexane; (c) and (d) 10ml of hexane.



(b) (c)

Fig. 6. EDS spectra of: (a) as received; (b) milled with 50ml of hexane and (c) milled with 10ml of hexane for 8 hours.

4. General Discussion

The morphology of the powder, the particle size, the crystallite size and the overall chemical composition of Cr_3C_2-Ni20Cr powders are affected by high energy milling. The nature of the milling media, used primarily to reduce contamination and to have a controlled milling atmosphere, influences these changes. Earlier studies indicated that milling efficiency in gaseous nitrogen was higher compared to that in hexane. In this investigation significantly lower amounts of hexane was used as the milling media and this has markedly increased the milling efficiency. Two different hexane contents were tried and milling efficiency was higher with the powder containing the lower hexane content. Both particle size and crystallite sizes decreased with reduction in the amount of hexane. This reduction in particle and crystallite size is related to increased impact energy transfer during the milling process. At higher hexane content the surfaces of the particles and the balls are coated with a thicker layer of hexane and this causes cushioning of particle-particle, ball-particle, ball-wall and particle-wall impacts. It is evident that the amount of hexane should be enough to coat surfaces and thereby decrease contamination without sacrificing impact energy transfer.
The high energy attritor tank is made of stainless steel and the balls used in the mill are of chromium steel. This as expected lead to an increase in Fe content of the high energy milled powders. Further increase in Fe content was observed with decrease in hexane content. This lends further proof to the extent of cushioning that hexane affects during milling.

5. Conclusions

High energy milling of Cr_3C_2-Ni20Cr powders with hexane as the milling media resulted in metal(alloy)-ceramic composites. The crystallite sizes were as low as 49 nm for Cr_3C_2 particles and 28 nm for Ni20Cr binder particles.

The volume of hexane used as the milling medium affects the final condition of the milled powder. Decrease in the amount of hexane decreased the extent of cushioning of impacts and decreased the particle and crystallite sizes considerably.

The increase in Fe content of milled powders and with decrease in hexane as the milling medium is considered normal in high energy milling. This increase in Fe content does not jeopardize the industrial use of milled nanostructured powders.

6. References

1. J.S. Benjamin, Metall. Trans., 1970, vol. 1, pp 2943-51.
2. J.S. Benjamin, Scientific American, 1976, vol. 234, pp 40-48.
3. J.S. Benjamin and T.E. Volin, Metall. Trans., 1974, vol. 5, pp 1929-34.
4. B.J. M. Aikin and T.H. Courtney, Metall. Trans., 1993, vol. 24A, pp 647-57.
5. J. He and J.M. Schoening, Materials Science and Engineering, A336 (2002),pp 274-319.
6. J. He, M. Ice, E.J. Lavernia, Metall. and Materials Transactions, vol. 31A, 2000, pp 555-64.
7. L.V. Ramanathan, A.Padial, J.R.Martinelli, N.B.de Lima and A.H.A Bressiani, Proc. 17 Brazilian Materials Science and Engineering conference, Foz de Iguacu, Brazil, Nov. 2006.
8. H. P. Klug and L.E. Alexander, X-ray Diffraction Procedures, Wiley, New York, 1974, 643.
9. E. Hellstern, H.J. Fecht, Z. Fu, and W.L. Johnson, J. Appl. Phys., 65 (1), 1989, pp 305-310.
10. C.C. Koch, O.B.Cavin, C.G. Mc Kamey, and J.O. Scarbrough, Appl. Phys. Letter, 43, 1983, pp 1017-1019.
11. E. Hellstern and L. Schultz, Appl. Phys. Letter, 48 (2), 1986, pp 124-126.
12. B. Huang, R.J. Perez, E.J. Lavernia, Materials Science and Engineering, A255,1998, pp 124-132.
13. E. Hellstern and L. Schultz, Appl. Phys. Letter, 49 (18), 1986, pp 1163-1165.
14. J. He, M. Ice, E.J. Lavernia, Nanostructured Materials, 10, 1998, 1271.
15. C. Suryanarayana, D. Mukhopadhyay, S.N. Patankar and F.H. Froes, Journal of Materials Research, 7, 1992, 2114.