Mechanical and Thermodynamic Properties of Cr_3C_2-25(Ni20Cr) Composite Powders produced by High Energy Milling

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ABSTRACT

Deformation energy is stored in the crystalline lattice of Cr_3C_2-25(Ni20Cr) powders, due to the high plastic deformation during high energy milling. X-ray diffraction measurements were used to determine the crystallite size as well as the microstrain in the crystalline lattice of Cr_3C_2-25(Ni20Cr) powders milled for different times. DSC analyses of these powders revealed a broad transformation, characteristic of a large exothermic reaction in the nanostructured powder. The enthalpy variation measured by the DSC equipment enabled determination of the deformation energy stored in the Cr_3C_2-25(Ni20Cr) powders milled for different times.

1. Introduction

Growing demand in recent decades for materials with enhanced properties has provided impetus for research and development in the field of nanostructured materials. There is increasing interest in the use of nanostructured coatings on components exposed to severe service conditions to prevent wear, erosion, corrosion/oxidation, separately or conjointly, and also to act as a thermal barrier in specific applications. Usually coatings prepared with nanostructured materials have exhibited higher hardness and strength compared with those prepared with conventional materials[1-4,7,9]. The feedstock for preparing nanostructured coatings is often obtained by high energy milling. This paper presents thermodynamic properties and structural features of Cr_3C_2-25(Ni20Cr) powder high energy milled for different duration.

It is well known that when metals are plastically deformed, most of the mechanical energy is converted into heat, but a small portion remains stored in the crystal lattice as "deformation enegy"[8]. The deformation energy stored in the Ni20Cr solid solution, the binding metallic phase in Cr_3C_2-25(Ni20Cr) composite, was determined from the enthalpy variation of this composite powder milled for different times. Cotterill[18] emphasized that this stored energy is important as it represents the energy of disorder produced by deformation (which is the driving force for the recovery and recrystallization processes), and that the main contributor to the total stored energy is generally associated with the increased number of dislocations, point defects and stacking faults, features of a material in the cold-worked state.

Additionally, due to the small crystallite size of nanostructured material, the grain boundaries contribute significantly towards the physical properties of the alloy (binder). Hence, the influence of grain boundaries on some mechanical and thermodynamic properties of Ni20Cr solid solution has been investigated in terms of the strain produced in the crystal lattice by the high energy milling process. This was done by determination of the deformation energy stored in the crystal lattice caused by the high mechanical deformation during the milling process, as well as by evaluation of the specific heat variation of Ni20Cr solid solution due to milling time. All these parameters were analyzed as a function of the reciprocal of crystallite size. As suggested by

Hellstern et al[6] this is reasonable, since the ratio of atoms close to grain boundaries to those within the crystal is proportional to 1/D. Additionally, it is emphasized that the milling time provides only an arbitrary scale for the evaluation of the material properties, since it depends strongly on the milling equipment, i.e., milling intensity, number of balls, size of the milling container, etc. Details about nanocrystalline powder synthesis and characterization are presented elsewhere [3,4, 15-17].

2. Materials and Methods

A high energy milling device (ZOZ) was used to mill Cr_3C_2-25(Ni20Cr) powders. As described elsewhere[15-17] the powder milling parameters were: 400 rpm, ball to powder ratio 10:1 and milling times of 2, 4, 8, 16, 20, 24, 32 and 64h. The milling was carried out in gaseous nitrogen media. Powder particle and crystallite sizes were determined using a particle size analyzer and by x-ray diffraction analysis, respectively. It should be noted that the x-ray diffraction analyses[5,14] were conducted using the Rietveld method for lattice refinement. The mean crystallite size as a function of milling time, as well as the microstrain (%) in the crystal lattice as a function of the crystallite size were determined using the Linear Fitting approach, the details of which can be found elsewhere[2,5]. Transmission electron microscopy (TEM) was used to study the microstructure of the milled powders. On the other hand, a scanning electron microscope (SEM), coupled to an energy dispersive spectrometer was used to examine the morphology and to determine the composition of the phases present in the milled powders (composite materials), as already described elsewhere[15-17]. The chemical composition of the powders was determined by x-ray fluorescence analysis. Differential scanning calorimetric (DSC) analysis[2,6,7] of powder samples milled for different duration was also carried out with a DSC-50 Shimadzu equipment. Powder samples of around 40mg were used with pure argon flux of 30 l/min. A heating rate of 10ºC/min was used in the temperature range 22 - 500ºC.

3. Results and Discussion
3.1. Chemical analysis

Similar to data previously reported[11,15-17], the Fe (at.%) content of the milled powders increased steadily with increase in milling time, the source being the stainless steel container and balls. However, it is important to note that all Fe atoms introduced in the composite are retained in solid solution in the NiCr alloy, as a result of the mecanical alloying process. This could be corroborated from the x-ray diffraction analysis results and TEM investigations.

3.2. Particle size, crystallite size and microstrain

The mean particle size of Cr_3C_2-25(Ni20Cr) powders decreased with milling time, as has been reported in the literature. Fig.[2-4,15-17].1a presents the mean particle size as a function of milling time. It is important to notice that particle size is an important operational variable, given that one of the requirements of the HVOF thermal spray process is that the feed stock powder must be in the range of 10 to 50 μm. On the other hand, x-ray difraction analyses of the milled powders were used to determine the crystallite size. Given that our interest in the present work is mainly related to microstrain produced in the crystal lattice due to severe plastic deformation introduced in the powders by high energy milling, as well as in the strain energy stored in the lattice as a result of the plastic deformation of the powders, the evaluation of crystallite size and microstrain (%) were performed using the Linear Fitting[2,5] approach, that is represented by equation (1),

$$\Delta(2\theta) \cos \theta \ = \ 2 \ \varepsilon \ \text{sen} \ \theta \ + \ 0{,}9 \ \lambda \ / \ D \qquad\qquad (1)$$

where D is the crystallite size, ε is the microstrain, λ is the wavelength (Cu target, λ = 1,54 A), Δ(2θ) is the full width at half maximum (FWHM) and θ is the diffraction angle.

As is well stablished in the literature, peak broadening verified in the x-ray diffraction spectra of milled powders gave clear evidence of structural changes that occurred in the powders. The five most important peaks of the NiCr alloy in the composite spectra were used to calculate the Full Width at Half Maximum (FWHM).

The mean crystallite size as a function of the milling time is shown in fig. 1b. It is evident that as milling time increased the crystallite size decreased[10,12,13]. In the initial stages of ball milling, crystallite size decreased rapidly to less than 50 nm. Further decrease in crystallite size to ~8 nm occurred steadily.
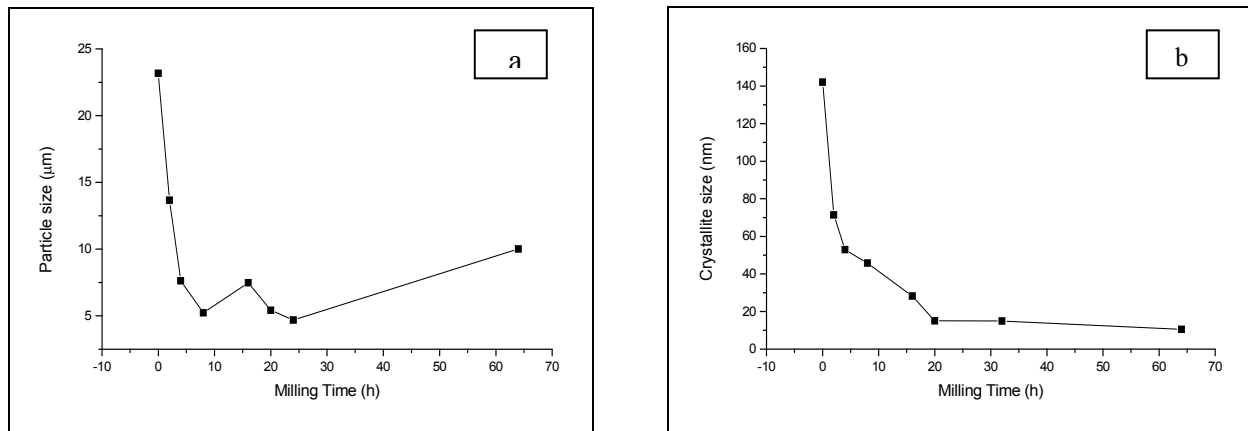

Fig. 1. Particle size (a) and crystallite size (b) variation as a function of milling time.

TEM analyses of the nanostructured powders provided direct observation of the crystallite size. Figures 2 (a) and 2 (b) show bright field images of nanostructured powders milled for 8 and 64 hours, respectively. The mean crystallite size observed by TEM was in good agreement with those determined by x-ray analyses.
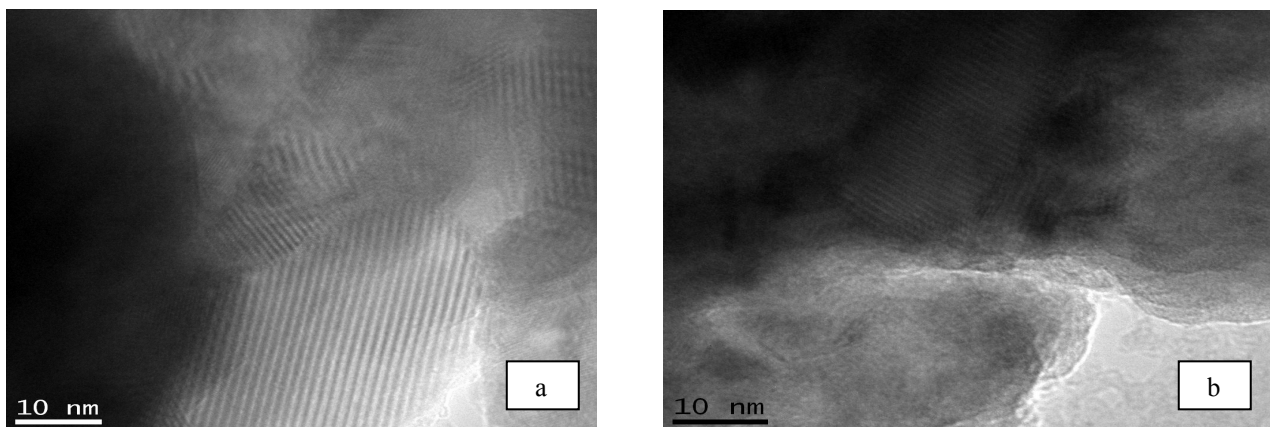

Fig. 2. TEM bright field image showing nanosized grains in powder milled for: (a) 8 hours, (b) 64 hours.

Fig. 3 shows the variation of microstrain as a function of the reciprocal of crystallite size. As expected, the deformation leads to a strong increase in atomic-level strains. It reaches a maximum microstrain value of 1.17% for a mean criystal size of 28 nm (equivalent to 16 hours of milling time). Further reduction in crystal size leads to a decrease in the strain verified in the crystal

lattice[2,6]. This effect is attributed to the reduction of dislocation density when crystallites become very small.

Another interesting result observed from the x-ray diffraction analyses results (Rietveld method) of the nanostructured powders was the variation in lattice parameter as milling time increased.
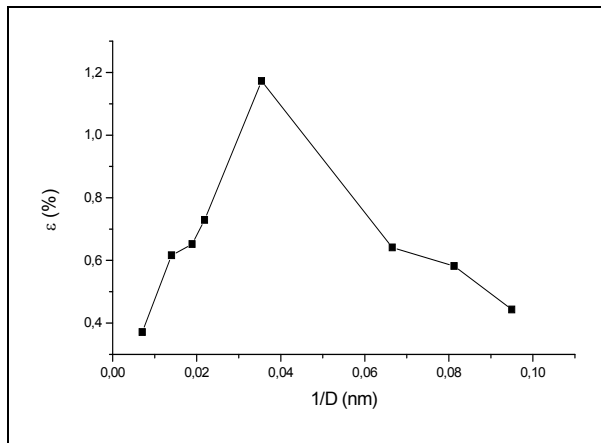

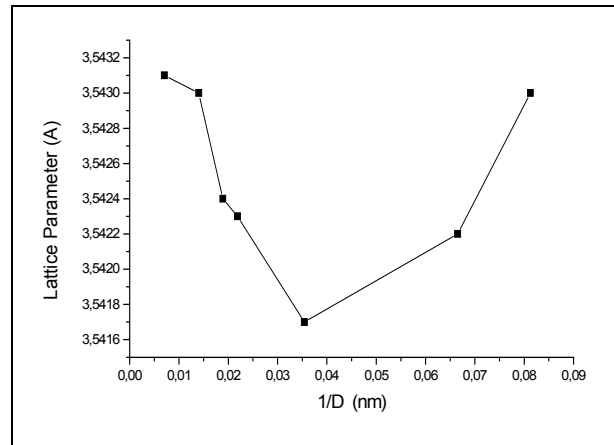Fig.3. Variation of microstrain as a function of reciprocal of crystallite size.

Fig. 4. Variation of lattice parameter as a function of reciprocal of crystallite size.

The referred variation of lattice parameter as a function of milling time is shown in the fig. 4, where it is possible to see that, in contrast to the behavior of microstrain in the crystal lattice, the lattice parameter reached a minimum in powders milled for the same time (when microstrain was maximum).

3.3. Enthalpy and specific heat variation

Regarding the energy stored in the crystal lattice, the DSC analyses performed in the nanostructured powders revealed the existence of a broad transformation in the temperature range
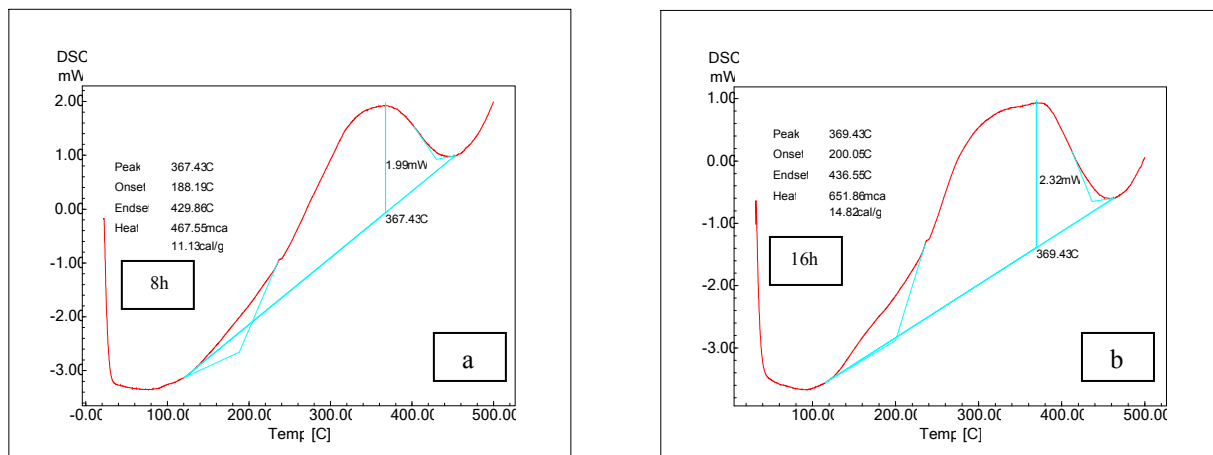

Fig. 5. DSC analysis of Cr_3C_2-25(Ni20Cr) powder milled for 8 hours (a) and 16 hours (b). Notice the broad transformation in the temperature range of about 120ºC to around 430ºC, illustrating the large exothermic reaction verified in the referred nanostructured material.

of about 120ºC to around 430ºC, indicating a large exothermic reaction that occurs in the referred nanostructured materials. Examples of such reactions are showed in the figures 5 (a) and 5 (b), which illustrate the condition for which the enthalpy variation reached a maximum, i.e., for

powders milled for 16 hours. In this condition the heat released in the exothermic reaction is of the order of 651 mcal. The same was observed with respect to the energy peak height, where the maximum value was 2.32 mW.

All DSC analyses results of the nanostructured powders milled for different times are shown in fig. 6. This figure clearly shows that enthalpy variation indeed reached a maximum for powders milled for 16 hours. Similarly, the energy peak height also revealed a maximum for powders milled for 16 hours, as presented in fig. 7.
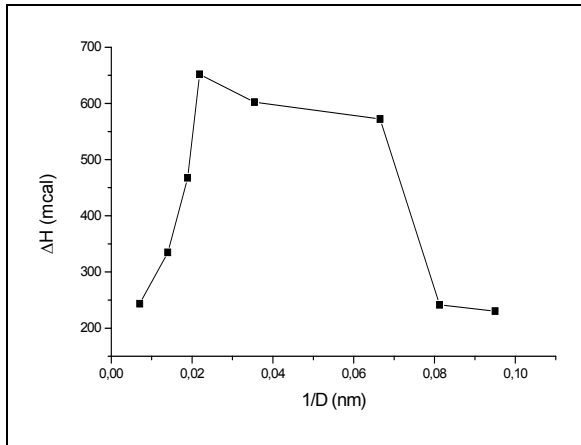

Fig. 6. Variation of enthalpy as a function of reciprocal of crystallite size. Notice that the maximum heat released occurred for powders milled for 16 hours.
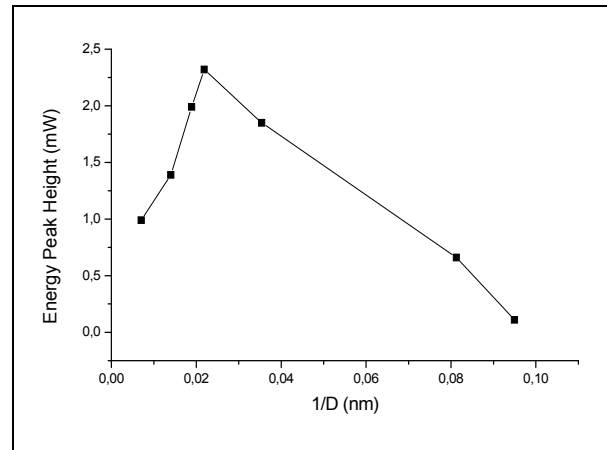

Fig. 7. Variation of the energy peak height as a function of reciprocal of crystallite size. Similarly, the maximum occurred for powders milled for 16 hours.

Concerning the calculation of specific heat variation, it is important to note that when pressure is constant (basic condition for tests performed in DSC equipment), $dQ = d(\Delta H)$ enabling evaluation of the variation in specific heat of the material, due to the severe plastic deformation introduced in the crystal lattice, using equation (2),

$$Q = m \, C_p \, \Delta T \qquad (2)$$

that can be rewritten as $\qquad \Delta C_p \; = \; (\Delta H) \, / \, m \, \Delta T \qquad (3)$
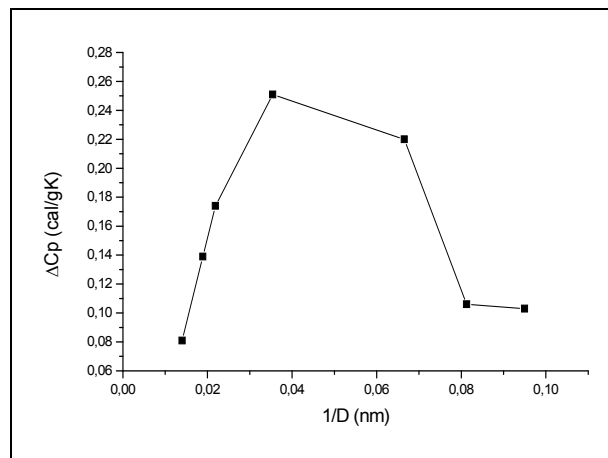

Fig. 8. Specific heat variation as a function of the reciprocal of crystallite size. Notice that the maximum variation occurred for crystallite size of 28 nm (powders milled for 16 hour as well).

Given that all values on the right side of equation (3) are known, for every powder milling condition, it was possible to calculate the specific heat variation of the nanostructured powders for each milling time. Fig. 8 presents the specific heat variation as a function of the reciprocal of crystallite size.

4. Conclusions

1. The peak broadening verified in the X-ray diffraction profiles of milled powders is a strong evidence of the structural changes occurred in that powders.
2. Cr_3C_2-25(Ni20Cr) powders submitted to high energy milling decreases crystallite size and increases the lattice strain.
   a. The crystallite size decreases to a certain value, around 10 nm, after which no further refinament is verified, even for longer milling times.
   b. The lattice strain at atomic level increases to a maximum for a crystallite size around 28 nm, further crystal size refinement leads to a decreases in lattice strain.
   c. The lattice parameter reaches a minimum at the same crystallite size that occurs the maximum for the microstrain in the atomic level.
3. The energy stored in the crystal lattice, due to severe plastic deformation, is released during heating, confirming the large exothermic reaction that occurs in the referred nanostructured materials.
   a. Enthalpy variation reaches a maximum for a crystallite size around 28 nm, i.e., for the powder that was milled for 16 hours.
   b. The maximum specific heat variation (ΔCp) occurred for crystallite size around 28 nm, i.e., for the powder milled for 16 hours.

5. References

1. J.S. Benjamin, Metall. Trans., 1970, vol. 1, pp 2943-51.
2. J. He and J.M. Schoenung, Materials Science and Engineering, A336 (2002), pp 274-319.
3. J. He, M. Ice, E.J. Lavernia, Metall. and Materials Transactions, vol. 31A, 2000, pp 555-564.4.
4. 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. 2006.5. H.
5. P. Klug and L.E. Alexander, X-ray Diffraction Procedures, Wiley, New York, 1974, 643.
6. E. Hellstern, H.J. Fecht, Z. Fu, and W.L. Johnson, J. Appl. Phys., 65 (1), 1989, pp 305-310.
7. J. He, M. Ice, E.J. Lavernia, Nanostructured Materials, 10, 1998, 1271.
8. G.E.Dieter, Mechanical Metalurgy, McGraw-Hill, 1976, 236.
9. B.H. Kear, L.E. McCandlish, Nanostruct. Mater. 3 (1993) 19 – 30.
10. J. He, E.J. Lavernia, J. Mater. Res. 16 (2001) 2724 – 2732.
11. C. Suryanarayana, Prog. Mat. Sci. 46 (2001) 1- 84.
12. J.S. Benjamin, Mater. Sci. Forum, 88-90 (1992) 1 – 18.
13. C.C. Koch, Nanostruct. Mater. 9 (1997) 13 – 22.
14. C. Suryanarayana, X-ray Diffraction – A Practical Approach, Plenum Press, New York, 1998.
15. C.A. Cunha, A.G.F. Padial, N.B. de Lima, J.R. Martinelli, O.V. Correa, L. V. Ramanathan, Materials Science Forum, Vols. 591-593 (2008), 282 – 288.
16. C. A. Cunha, N.B. de Lima, J. R. Martinelli, A. H. A. Bressiani, A. G. F. Padial, L. V. Ramanathan, Materials Research, Vol. 11, No. 2, (2008), 137-143.
17. A. G. F. Padial, C. A. Cunha, N.B. de Lima, J. R. Martinelli, L. V. Ramanathan, Materials Science Forum, Vols. 660-661 (2010), 379-384.
18. P. Coterril, PR. Mould, Recrystallization and Grain Growth in Metals, John Wiley & Sons, New York, 1976.