



STRUCTURAL AND THERMODYNAMIC PROPERTIES OF $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$ COMPOSITE POWDERS PRODUCED BY HIGH ENERGY MILLING

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Abstract

Chromium carbide-nickel chromium ($\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$) cermet powders were high energy milled to produce nanocrystalline powders. This form of milling causes severe plastic deformation and energy to be stored in the crystalline lattice. The crystallite size and microstrain in these nanostructured powders were determined as a function of milling times by x-ray diffraction analyses. DSC analyses of the milled powders revealed a broad transformation, characteristic of a large exothermic reaction in the nanostructured powder. The deformation energy stored in the $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$ powders milled for different times was determined by measurement of the enthalpy variation, performed in a DSC equipment. These measurements also enabled calculation of the specific heat variation in these powders.

Keywords: $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$, crystallite size, microstrain, thermodynamic properties.

1. INTRODUCTION

This paper presents the thermodynamic properties and structural features of nanostructured $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$ powder prepared by the high energy milling. 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 energy”⁽¹⁾. In milled $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$, deformation energy is primarily stored in the Ni20Cr solid solution and this was determined from the enthalpy variation of this composite powder milled for different times⁽²⁾. Since this microstrain is responsible for lattice deformation, determination of the deformation energy stored in the crystal lattice enables evaluation of the specific heat variation of Ni20Cr due to milling time. All these parameters were studied as a function of the reciprocal of crystallite size ($1/D$). This has basis on the suggestion that supports the idea that the ratio of atoms close to grain boundaries to that within the crystal is proportional to $1/D$ ⁽³⁾. Milling time provides only an arbitrary scale to evaluate material properties. Details about nanocrystalline powder synthesis and characterization are presented elsewhere^(2,4,5).

2. OBJECTIVE

The objectives of this investigation were to: (a) determine the crystallite size as well as the microstrain at the atomic level in $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$ powders that were high energy milled for different times; (b) determine the “deformation energy” stored in the crystal lattice of the Ni20Cr solid solution, by measuring the enthalpy variation of powders milled for different times.

3. MATERIAL AND METHODS

A high energy milling device (ZOZ) was used to mill the $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$ powders. The main powder milling parameters were: 400 rpm, ball to powder ratio 10:1 and gaseous nitrogen media, with milling times of 2, 4, 8, 16, 20, 24, 32 and 64h. Further details can be found elsewhere^(6,7). The crystallite size and microstrain were measured by x-ray diffraction analyses using the Rietveld method for lattice refinement^(8,9). 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, details of which can be found elsewhere^(2,8,9). Differential scanning calorimetric (DSC) analyses^(2,3,10) of powder samples milled for different times was 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 10°C/min was used in the temperature range 22 - 500°C.

4. RESULTS AND DISCUSSION

4.1. Crystallite size and microstrain.

Figs.1a and 1b present the mean crystallite size and the microstrain produced in the crystal lattice due to severe plastic deformation introduced in the powders during high energy milling. Crystallite size and microstrain (%) were determined using the Linear Fitting approach, represented by the equation: $\Delta(2\theta) \cos \theta = 2 \varepsilon \sin \theta + 0,9 \lambda / D$, where D is the crystallite size, ε is the microstrain, λ is the wavelength (Cu target, $\lambda = 1,54 \text{ \AA}$), $\Delta(2\theta)$ is the full width at half maximum (FWHM) and θ is the diffraction angle.

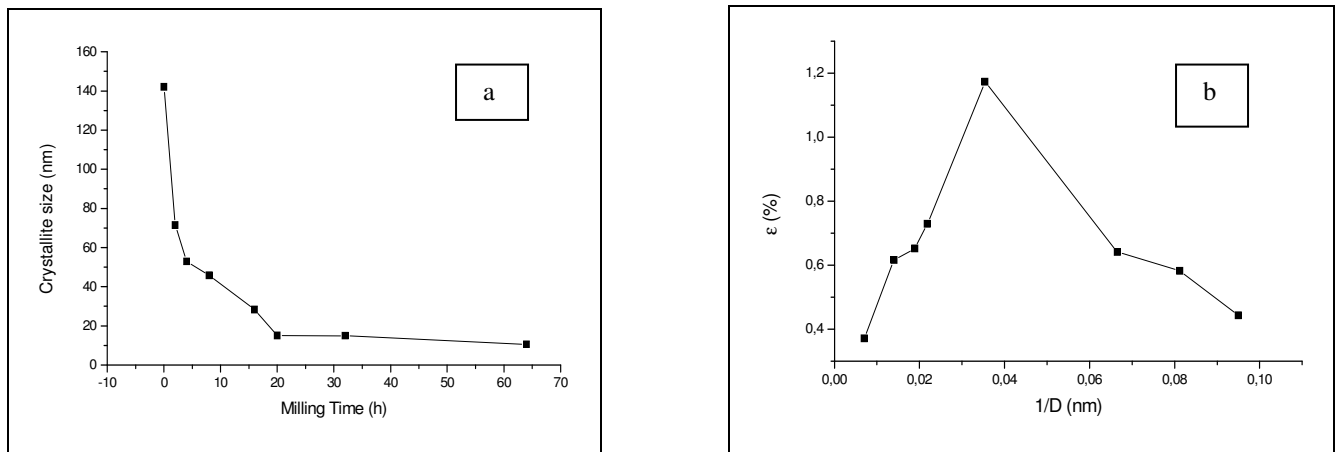


Fig. 1: (a) Mean crystallite size and (b) microstrain (%) of the nanostructured $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$ powders.

It is evident that as milling time increased the crystallite size decreased⁽²⁻⁷⁾. In the initial stages of milling, crystallite size decreased rapidly to less than 50 nm. Further decrease in crystallite size to ~10 nm occurred steadily. On the other hand, the microstrain (%) reached a maximum for a mean crystallite size of ~28 nm (16 hours of milling time). Further deformation lead to a decrease in microstrain (%) in the crystal lattice.

4.2. Enthalpy and specific heat variation.

In terms of energy stored in the crystal lattice^(2,3,11), DSC analyses of the nanostructured powders revealed the existence of a broad transformation in the temperature range of ~120°C to ~450°C, indicating the occurrence of a large exothermic reaction in the nanostructured materials, as shown in Fig. 2a. All the DSC analyses results of the Cr₃C₂-25(Ni20Cr) nanostructured powders are summarized in Fig. 2b, which clearly shows that enthalpy variation indeed reached a maximum for powders milled for 16 hours.

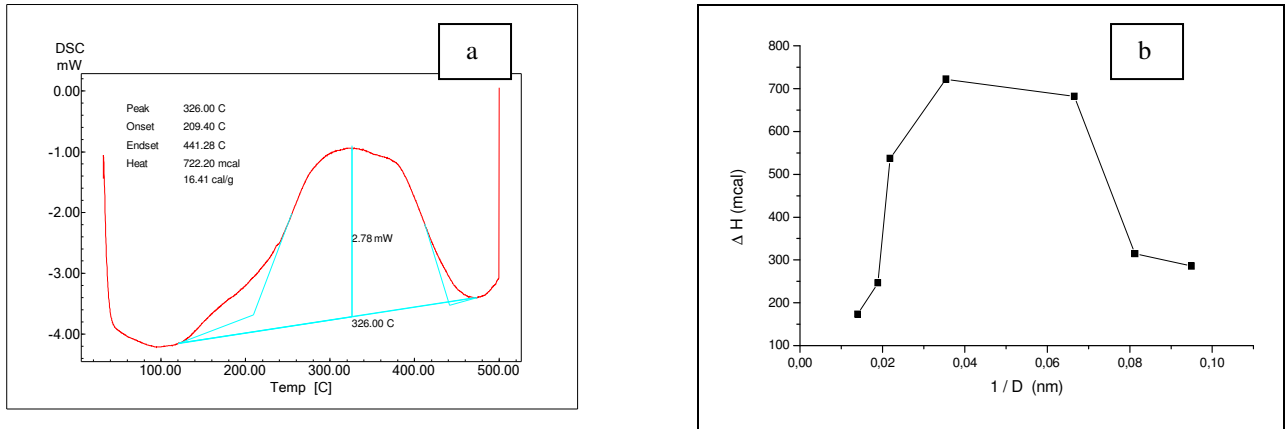


Fig. 2. (a) DSC curves showing enthalpy variation observed in powder milled for 16 hours. Notice the broad transformation indicating a large exothermic reaction. (b) Enthalpy variation as a function of reciprocal of crystallite size. The maximum heat release occurred from powders with a mean crystallite size around 28 nm (milled for 16 hours).

In a similar manner, the energy peak height also revealed a maximum for powders milled for 16 hours, as shown in Fig. 3a. Regarding calculation of specific heat variation^(10,12), it is important to note that when pressure is constant (basic condition for DSC tests), $dQ = d(\Delta H)$ and this enables determination of the variation in specific heat of the material, due to severe plastic deformation introduced in the crystal lattice, using equation: $Q = m C_p \Delta T$, that can be rewritten as: $\Delta C_p = (\Delta H) / m \Delta T$. Given that all values on the right side of equation (2) are known, for every milling condition, it was possible to calculate the specific heat variation of the nanostructured powders for each milling time. Fig. 3 presents the specific heat variation as a function of the reciprocal of crystallite size.

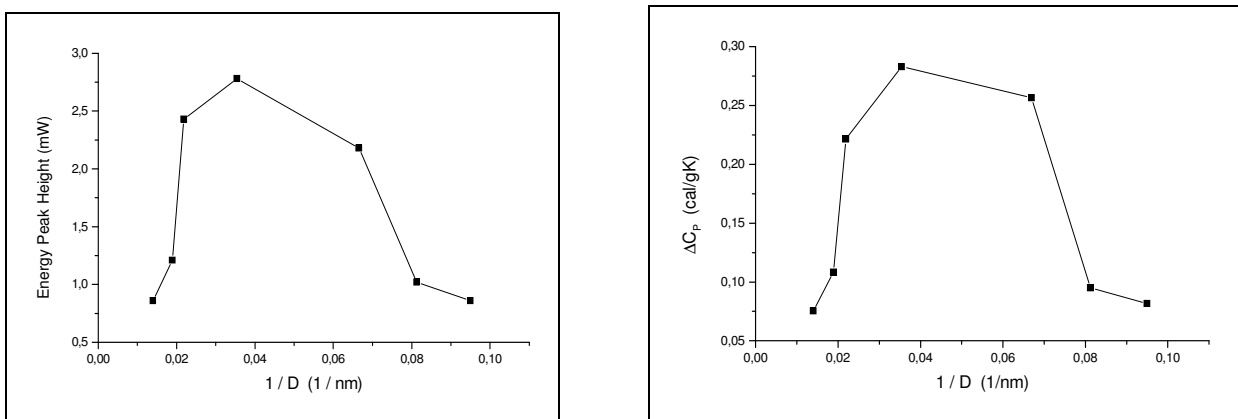


Fig. 3. (a) Energy peak height and (b) Specific heat variation as a function of reciprocal of crystallite size. In a manner that is quite similar, the maximum energy peak height and the specific heat variation occurred for powders with crystallite size around 28 nm (16 hours of milling time).



CONCLUSIONS

1. High energy milling of $\text{Cr}_3\text{C}_2\text{-25(Ni20Cr)}$ powders decreased its crystallite size and increased lattice strain. The crystallite size decreased rapidly to ~ 50 nm, after which further decrease in crystallite size to ~ 10 nm occurred steadily. The lattice strain at the atomic level increased to a maximum for crystallite size of ~ 28 nm and further crystal size refinement brought about decrease in lattice strain.
2. Enthalpy variation reached a maximum for crystallite size of ~ 28 nm (corresponding to 16 hours of milling) and the maximum specific heat variation (ΔC_p) also occurred for crystallite size of ~ 28 nm.

5. REFERENCES

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