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Effect of microstructure on thermal expansion behaviour of nanocrystalline metallic materials

Stefano Gialanella · Francesco Marino

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Abstract Materials properties, among which thermodynamic ones, are influenced by microstructural features. This is so also in the case of nanocrystalline materials, featuring average grain size below 100 nm. A reduced grain size involves that significant fractions of atoms are localised in grain boundary regions and this has remarkable effects on the resulting thermodynamic properties, like heat capacity, transition temperatures, coefficient of thermal expansion, etc. In the present work we consider the thermal expansion behaviour of ball-milled nanocrystalline metallic powders using dilatometric measurements. High-energy ball-milling, that is capable to achieve extremely high deformation degrees, induces in the milled powders microstructural defects, like vacancies, antisites, dislocations and planar faults. Another effect of milling is the reduction of the crystallite size, that, in the long run, may reach the nanometric range. In view of the microstructural changes that can be brought about by milling and of the numerous transformations occurring during the dilatometric runs, a comparative study has been conducted on intermetallic, NiAl and Ni_3Al, and on a pure metal, nickel, powders. The results emerging from the experimental investigation are quite complex, owing to the complex defect structures that are present in the ball-milled powders. It turns out that the thermal expansion coefficient of the nanocrystalline powders increases as the average grain size is reduced. However, when the average grain size achieves very low values, the strain relaxation of the crystalline lattice and the rearrangement of grain boundary regions result in a reduction of the thermal expansion coefficient. Another aspect that emerges from the dilatometric curves is the interplay between recrystallization and reordering, i.e. the re-establishment of the long-range order in the intermetallic powders, that had been partially or fully eliminated by ball-milling.

Introduction

Nanocrystalline materials (nXMs), featuring average grain size below 100 nm [1], display peculiar properties depending on their actual microstructure. A reduced grain, or domain, size involves that significant fractions of atoms are localised in grain boundary regions. It has been evaluated that, assuming an equiaxed grain size of 5 nm and a grain boundary width of 1 nm, the volume occupied by grain boundary atoms would account for as much as 50 vol% of the overall volume [2]. Therefore, it is obvious that grain boundary regions would significantly influence materials properties, and, in particular, the thermodynamic ones. First of all, phase stability of nXMs should be described by an appropriate expression of the Gibbs free energy function, reliably accounting for the specific features of nXMs, like the elevated concentration of unsaturated and distorted atomic bonds, interstitials, vacancies and other microstructural defects, that, owing to the reduced grain size, may be present in comparable concentrations as the bulk atoms. In some models, like the one proposed for nanograined alloys [3], the energy contribution of grain boundaries to the total free energy can be expressed by a positive surface energy term.

This paper is dedicated to the memory of our dear colleague Rocco Delorenzo.

S. Gialanella (✉)
Dipartimento di Ingegneria dei Materiali e Tecnologie
Industriali, Università di Trento, 38050 Mesiano, Trento, Italy
e-mail: stefano.gialanella@ing.unitn.it

F. Marino
Dipartimento di Scienza dei Materiali e Ingegneria Chimica,
Politecnico di Torino, C.so Duca degli Abruzzi 24,
10129 Torino, Italy

For the calculation of thermodynamic properties, a general approach based on a universal equation of state has been proposed by Fecht [4, 5]. According to this approach, a positive expansion in the atomic volume, determined by the material internal pressure, has been foreseen with reference to several nanocrystalline metallic materials. Another result is the existence of a critical atomic volume, beyond which negative bulk modulus values would result. Moreover, the irregular structure of the atomic bonds in grain boundary regions and the resulting anharmonicity in the interaction potential curves give generally place to higher coefficients of thermal expansion (CTE) for grain boundaries as compared to lattice values. For instance, an experimental investigation carried out on copper samples, demonstrated that the CTE of grain boundaries can be from 2.5 up to 5 times larger than the bulk values, depending on the assumptions made on the thickness and elastic properties of grain boundary [6]. According to this picture, the CTEs of single crystals are expected to be lower than the CTE values for polycrystalline samples of the same materials. An even larger increase in CTE is thus to be expected for nX materials, owing to their particularly high concentration of grain boundaries. Actually, if other microstructural parameters than grain boundaries are considered, the observed behaviour of CTE can be relatively more complex, as displayed by systematic investigations carried out on Al, Ti [7], Ni, Cu [8] and Pd [9] thin film samples.

In the present work we consider the thermal expansion behaviour of ball-milled nanocrystalline metallic and intermetallic powders. Ball-milling, a high energy tool used to achieve extremely elevated deformation degrees even in comparatively brittle intermetallics, induces in the milled powders microstructural defects, like vacancies, antisites, dislocations and planar faults. Another effect of milling is the reduction of the crystallite size, that, in the long run, may lead to nanometric grain size [10]. In view of the wide range of microstructural changes that can be brought about by milling and of the numerous transformations occurring during the dilatometric runs a comparative study has been conducted on intermetallic and a pure metal powders.

A dilatometric approach is used to study the thermal stability of the nanograined milled powders and to estimate the values of the thermal expansion coefficients corresponding to different microstructural conditions.

Experimental

Three different powders have been considered for this study. Two intermetallic powders: Ni_3Al and NiAl and an elemental nickel powder. The Ni_3Al-base powder has been supplied by J.R. Knibloe and R.N. Wright, who conducted a thorough investigation on these gas-atomised powders and their sintering behaviour [11]. The NiAl and Ni powders are commercial products obtained by water and gas atomisation, respectively. In Table 1 additional information on these powders is provided.

Table 1 Chemical compositions of the powders used for ball-milling experiments

Powder	Ni (at.%)	Al (at.%)	Other
Nickel	>99.99	–	Minor impurities
Ni_3Al	76.6	23.3	0.1 at.% B
NiAl	47.88	52.22	Minor impurities

Powders have been ball-milled for times up to 96 h in a vibratory mill, that has been used as it allows for pure gas and vacuum connections. In this case milling has been conducted under a static Ar-gas pressure, that has been backfilled after the milling jar has been evacuated with a rotary pump and purged several times with the same inert gas. For all milling experiments we used grinding media, i.e. vials and balls, made of Cr stainless steel. Through a suitable selection of processing parameters, like ball to powder weight ratio, vibration amplitude and frequency, etc., it has been possible to limit the contamination from the grinding media. In fact, not even in the specimens milled for the longer times, contamination elements have been detected using energy dispersive X-ray spectroscopy analyses. X-ray diffraction was used to follow the microstructural evolution upon milling, as already reported in former studies [12–14].

As concerns dilatometry, an instrument equipped with a sample holder specifically designed for loose powder specimens was used. To prevent oxidation, the dilatometric runs have been conducted under an inert gas, i.e. argon, flows, from room temperature up to maximum temperatures of 500 or 640 °C, according to the specific kind of powder. Dilatometric tests have been conducted with heating and cooling rates of 5 $°C\ min^{-1}$, although during cooling this rate could only be maintained down to temperatures of about 250 °C, as at that point the spontaneous cooling of the instrument became slower than the set rate. In all cases, at the end of the thermal measurements samples were still in the initial condition of loose powders. This was to be expected, in view of the significantly higher temperatures and longer times, as compared to those of the dilatometric tests, required to promote sintering processes. The CTEs of the different branches of the dilatometric curves have been evaluated from their slopes with an estimated error of $\pm 0.1\ °C^{-1}$.

Results

The effect of the microstructural modifications induced by ball-milling on the dilatometric response of the Ni_3Al

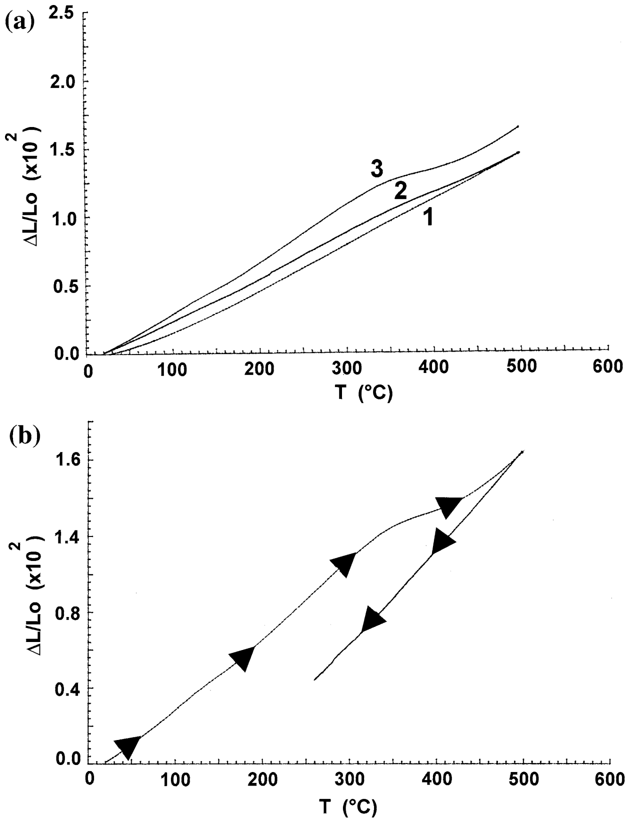

Fig. 1 **a** Dilatometric curves of the Ni_3Al powder samples that have been milled for short times: curve 1 refers to a powder milled for 10 min.; curve 2 for 30 min and curve 3 for 120 min. The following CTE values have been estimated for each one of the curves over the temperature interval 20–300 °C: (1) 8.1×10^{-6} °C^{-1}; (2) 8.5×10^{-6} °C^{-1}; (3) 10.2×10^{-6} °C^{-1}. **b** Graph displaying also the cooling branch for curve 3 in Fig. 1a

powders is displayed in Fig. 1a. The original powder, when milled for increasing time, displays a progressive increase in the slope of the dilatometric curves from room temperature up to 500 °C. Curve 1 in Fig. 1a corresponds to a sample that has been milled for just 10 min. From the slope of the curve the value of 8.1×10^{-6} °C^{-1} for the thermal expansion coefficient has been obtained. The monotonic, almost linear, behaviour of this curve is lost after 30 min milling (curve 2, Fig. 1a). The slope of the curve is now slightly steeper, with a CTE of 8.5×10^{-6} °C^{-1} for temperatures up to 300 °C. At this temperature, a deflection is visible in the dilatometric curve. This effect is even more visible in curve 3 of Fig. 1a, obtained with a powder that has been milled for 120 min. In this case, a CTE of 10.2×10^{-6} °C^{-1} has been measured with reference to the first linear part of the curve. This effect is irreversible, is fully recovered after the first heating and it is not visible in the cooling run. This is clearly shown by Fig. 1b, where the first heating of the sample milled for 120 min (curve 3 in Fig. 1a) is followed by an immediate cooling. In this latter thermogram the material displays a similar behaviour as that of the unmilled powder, for which a thermal expansion coefficient of 17.0×10^{-6} °C^{-1} was estimated [12].

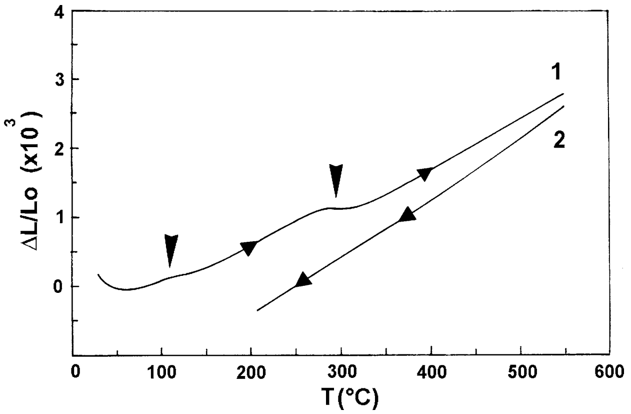

Fig. 2 Dilatometric heating curve (1) of the Ni_3Al powder milled for 96 h, displaying at least a couple of transformations (*arrowed*), starting at about 270 °C. The transformations are irreversible as they are not present any longer in the cooling curve (2)

Ni_3Al powder milled for 96 h has been prepared and provided the dilatometric curves displayed by Fig. 2. The step-like transformation, already visible in Fig. 1a (curve 2 and 3), is now very pronounced and has an estimated onset temperature of 280 °C. Its irreversibility is confirmed by the lack of any signal in the cooling branch (Fig. 2, curve 2).

The set of subsequent heating runs carried out on the same Ni_3Al milled sample and displayed in Fig. 3 provides a further confirmation of the irreversible character of the transformation, that indeed is observed during the first heating only. In fact, the second and third runs, carried out without removing the powder specimen from the dilatometer (Fig. 3, curves 2 and 3, respectively) are nearly fully coincident and have a monotonic trend not showing any inflection as the one visible in curve 1. Still referring to Fig. 3, another aspect that deserves to be remarked is the increase in the slope of the dilatometric curves 2 and 3 as compared to the slope of curve 1.

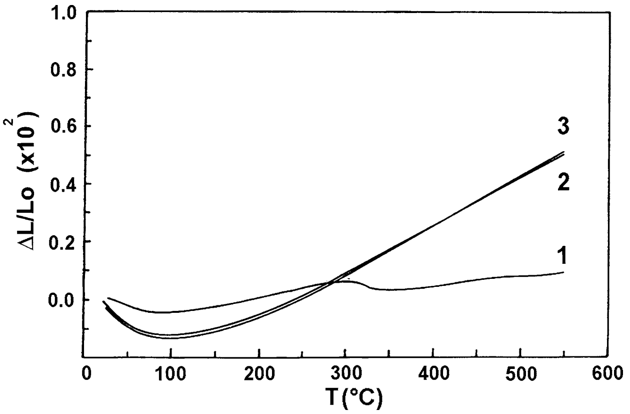

Fig. 3 Three dilatometric heating curves of the Ni_3Al powder milled for 96 h, acquired without removing the sample from the dilatometer

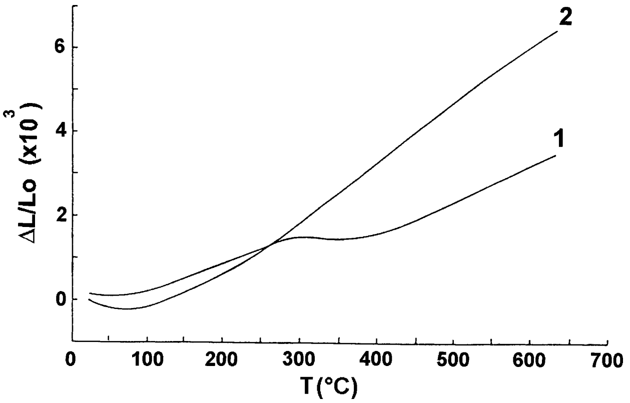

Fig. 4 Two dilatometric heating curves of the NiAl powder milled for 96 h. Thermograms have been acquired without removing the sample from the dilatometer

Dilatometric results very similar to those just discussed for the Ni_3Al material have been obtained with the NiAl sample, the other intermetallic phase considered in the present study. This is shown by Fig. 4. The first heating run still features a contraction, starting at a temperature of 295 °C. In the second heating cycle, the step-like transformation has disappeared and again we have a curve with a larger slope than in the original, ball-milled condition. The situation achieved after the second heating cycle is stable and no significant changes have been observed after any further treatment conducted on the same NiAl sample.

The dilatometric results presented so far refer to intermetallic phases: Ni_3Al and NiAl and the relevant values of the CTE corresponding to different conditions achieved after milling and dilatometric runs are summarised in Table 2.

To complete the picture we have performed the same milling experiment on a pure metal specimen, i.e. a pure nickel powder. Nickel has been selected for its affinity to the two aluminides and for its thermal stability over the temperature interval interesting for the dilatometric tests. Figure 5 shows two dilatometric heating curves obtained from a nickel powder sample, milled for 96 h under the same conditions as those used for the Ni_3Al and NiAl intermetallic phases. Apart from an instrumental offset, the two thermograms display no major differences and different CTE regimes can be identified. The corresponding values of the CTE measured over different temperature intervals are listed in Table 3.

Table 2 Coefficients of thermal expansion of the Ni_3Al and NiAl powders, estimated from the curves in Figs. 3 and 4, respectively

Sample	CTE ($°C^{-1}$)	
	1st heating ($\times 10^{-6}$)	2nd heating ($\times 10^{-6}$)
Ni_3Al	4.0	17.0
NiAl	8.4	10.5

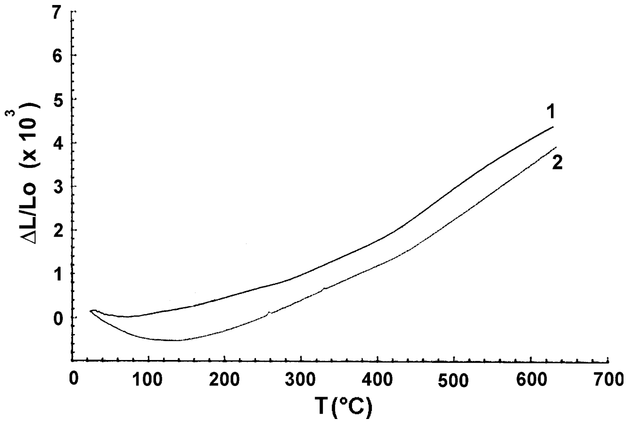

Fig. 5 Two dilatometric heating curves of the Ni powder milled for 96 h. Thermograms have been acquired without removing the sample from the dilatometer

Table 3 Coefficients of thermal expansion of the pure nickel powder, estimated from the curve in Fig. 5

Temperature range (°C)	CTE ($°C^{-1}$) ($\times 10^{-6}$)
150–350	5.6
450–640	11.5
Bulk Ni[a]	12.4

[a] The literature value of the CTE for bulk microcrystalline nickel is also reported for a comparison [16]

General discussion

Dilatometric tests have been used to investigate the transformations that can be thermally induced in ball-milled metallic powders. An effect of prolonged milling, that has been observed in all samples, is a reduction of the average crystallite size down to the nanometric range. The ultimate values of crystallite size, determined from X-ray diffraction results, were 12 nm for the Ni and Ni_3Al powder, larger for the NiAl material, i.e. 25 nm, as published in previous works on the same materials considered in the present investigation [12–14]. The two intermetallic phases displayed also changes in the degree of long-range order, that went to zero in the Ni_3Al powder after the 96 h milling, starting from a fully ordered condition in the unmilled powder. Just a slight reduction in the long-range order parameter was measured instead in the NiAl material: from the initially ordered condition, before milling, a long-range order parameter equal to 0.94 was measured in the sample milled for 96 h.

In view of the microstructural features that have been induced into the materials by high-energy ball-milling, it is to be expected that the annealing treatments associated with the dilatometric tests should promote a recrystallisation of the nanometric domains and the re-establishment of a correct lattice site occupation in the intermetallic phases with a consequent increase in the long-range order parameter. In the cited investigation on disordering and reordering of Ni_3Al [12], two transformations have been recorded in the dilatometric heating curve (arrowed in the heating thermogram in Fig. 2). As reported, the low temperature transformation has no effect on the microstructure of the intermetallic powder, as it leaves nearly unchanged the average crystallite size and the lattice strain [12]. The same can be said for the long-range order parameter, that was still equal to zero after this low temperature transformation. In view of these results, the transformation was associated to short-range re-ordering. This interpretation is also supported by the results obtained by Anthony et al. [15] from extended electron energy loss fine structure measurements, that displayed in an initially Ni_3Al-disordered thin film the constitution of the correct atomic environment around each atomic species after annealing treatments at temperatures not exceeding 200 °C. A significant increase in the long-range order parameter was observed in the Ni_3Al powder sample after it was heated up to 600 °C. Although the long-range order parameter resulted to be lower than the pre-milling value, the higher temperature transformation can be interpreted as a reordering process, starting from the metastable disordered configuration achieved with milling. Incidentally, it is worth noting that a similar contraction in the dilatometric curve has been also reported for another $L1_2$ ordered alloy, $(Co_{0.78}Fe_{0.22})_3V$, isomorphous to N_3Al, disordered by water quenching [16]. The contraction observed when the intermetallic phase goes from a disordered to an ordered state, would agree with the establishment of a more efficient atomic packing in the long-range ordered structure. The curves in Fig. 1a display how with increasing milling time and, therefore, with an increasing degree of disorder induced into the material, a progressively more intense reordering transformation is observed. An interesting aspect emerging from a comparison of the dilatometric curves in Figs. 1 and 2 concerns the evolution of the coefficient of thermal expansion with milling time (Table 2). In Fig. 1a, a progressive increase of the slopes of the dilatometric curves referred to samples milled for increasingly long times can be noticed. Such an increase can be ascribed to the reduction, upon milling, of the grain size and the corresponding increase in the grain boundary concentration. As recalled, the contribution of grain boundaries to the overall CTE has been directly measured on microcrystalline copper samples and the higher values than bulk CTEs have been justified in terms of anharmonic atomic vibrations determined by the structural disorder of these regions [6].

A different trend in the CTE has been observed in all powders, Ni, NiAl and Ni_3Al, milled for 96 h. In fact, lower CTE values have been measured, as displayed by the dilatometric runs in Figs. 3, 4, for Ni_3Al, NiAl, respectively and Table 2. For the nickel powder the reader is referred to the values of CTE inferred from the curve in Fig. 5 and listed in Table 3, together with the CTE literature value for bulk microcrystalline nickel [17]. From these data it turns out that over all temperature ranges the CTEs for milled nickel stay higher than the CTE for the microcrystalline metal.

In the thermograms of Ni_3Al and NiAl it is evident that the slopes of the first heating runs are lower than those of the subsequent ones, carried out in each case on the same specimen, without removing it from the dilatometer. A similar behaviour has been previously reported for ball-milled iron powders [18]. A drop in the CTE was observed in heavily milled powder specimens whereas higher CTEs were obtained for samples milled to a lower extent. The reduction in the CTE values has been interpreted as due to a grain boundary relaxation. The relief of the stresses associated not only to the strain in the grain boundary regions, but also within the nanometric crystallites has been proposed as a further factor that may influence the thermal properties, among which CTE, of nanocrystalline materials [19]. This sort of recovery is commonly encountered in heavily milled materials and may be enhanced by the surface energy term associated with crystallite and dislocation cell boundaries [20, 21].

Regarding the higher temperature (around 300 °C) transformation recorded in the dilatometric heating curve in Figs. 1 and 2, it must be noticed that the observed contraction does not involve re-ordering only, but also a partial recrystallisation of the deformed grains [12]. In this view, the recorded contraction is not to be associated to the more efficient spatial occupation of the ordered state only, but also to the annihilation of lattice defects introduced with ball-milling. Of course, these phenomena are favoured by the diffusion routes provided by the high concentration of grain boundaries, that in the process are eliminated too. The concurrence of different phenomena in determining the transformations observed in the dilatometric curves is also evident in case of the NiAl material. Although the NiAl powder even after prolonged ball-milling results only slightly disordered, it still displays a significant contraction in the relevant dilatometric curve (Fig. 4, curve 1). Therefore, we propose that the dilatometric signals recorded with both NiAl and Ni_3Al around 300 °C represent a combined diffusive transformation, involving the microstructural defects introduced into the milled alloys. To support this idea, we recall an already published calorimetric investigation on these same materials [22–24]. The calorimetric data, displaying a similar trend for the two alloys, indicate for both NiAl and Ni_3Al the existence of an exothermic reaction, having a maximum peak value that would exactly correspond to the dilatometric transformations.

The dilatometric heating curves for pure nickel (Fig. 5) showed quite different trends as compared to the intermetallic materials. In particular, the contraction observed around 300 °C, that has been associated to a concurrent set of transformations, is absent in the thermograms of the pure metal powder. Moreover, the two curves in Fig. 5, displaying the thermal expansion behaviour of nickel powders during two subsequent heating runs, have a very similar aspect, as an indication that the first heating cycle, up to a temperature of 600 °C, is not significantly changing the microstructure of the material with respect to the condition present after ball-milling. Ball-milling techniques are capable to introduce very high concentrations of deformation defects. In elemental powders, featuring high concentrations of grain boundaries and dislocations, vacancy annihilation, diffusive processes, like recovery and recrystallisation, can dynamically occur during ball-milling itself at comparatively low temperatures, e.g. room temperature [25]. This spontaneous recovery would be more probable in pure nickel than in the other multielemental compounds considered in the present contest, for the lack of any chemical constraint for the atomic lattice occupation in case of the pure metal. The dynamic recovery of deformation defects occurred during milling in the nickel powder may explain the lack of the recrystallisation contraction in the two dilatometric curves in Fig. 5.

Final comments and conclusions

The present study is focussed on the dilatometric behaviour of nanograined metallic powders and is meant to complete previous investigations carried out on similar samples using calorimetric and X-ray diffraction methods. The nanometric grain size has been attained by high-energy ball-milling and the dilatometric tests have been carried out to follow the recovery kinetics of the differently milled powders.

The dilatometric thermograms of the intermetallic phases display signals that have been associated to diffusive transformations from the metastable initial condition resulting from prolonged ball-milling. These transformations involve, to different extent for the different phases, annihilation of point defects, recrystallisation and reordering. In the case of the pure ball-milled nickel powder, a different dilatometric behaviour has been observed and ascribed to a partial dynamic recovery, occurring during milling, of the microstructural defects introduced by the intense deformation.

Another aspect that emerged from the dilatometric analyses concerns the CTE values. For the intermetallic powders milled for 96 h, the first heating runs provided in all cases values lower than those measured on the same specimens after subsequent anneals(Table 2), although we actually observed an increase of CTE in Ni_3Al powder milled only for short times (see text and caption of Fig. 1a).

For pure nickel, no significant changes have been noticed between the first and the following dilatometric heating. In all cases, the measured CTEs resulted below the findings of formerly reported theoretically and experimentally estimated values for CTE for microcrystalline nickel [8]. Incidentally, these lower values of CTEs, seem to be even in apparent contrast with the higher CTE values expected for nanocrystalline systems [26, 27]. However, when dealing with heavily deformed nanograined powders, as it is the case of high-energy ball-milled materials, dynamic recovery processes may be triggered by the high concentrations of defects achieved during milling. This recovery drives the milled material to a less defective microstructure, as appears to be the case of ball-milled nickel powder.

As reported, from the interplay of these mechanisms, different dependences of the CTE from the crystallite size and defects structures may originate [8]. To complete the picture, other important parameters will probably have to be accounted for to fully explain the observed experimental results present in the literature. For instance, Zhu et al. [28] have found a dependence of the CTE and other materials parameters on the ratio of the grain boundary energy to the surface energy.

Therefore, further in depth systematic studies would be required and help understanding important aspects of this large and increasingly important class of materials, i.e. nXMs, as already highlighted in a review paper concerning electrodeposited and consolidated nanograined materials [29].

References

1. Gleiter H (2000) Acta Mater 48:1
2. Siegel RW, Hahn H (1987) In: Yussouff M (ed) Current trends in the physics of materials. World Science Publications, Singapore
3. Weissmuller J (1994) J Mater Res 9:4
4. Fecht H (1990) Phys Rev Lett 65:610
5. Fecht H (1990) Acta Metall Mater 38:1927
6. Klam HJ, Hahn H, Gleiter H (1987) Acta Metall 35:2101
7. Fang W, Lo C-Y (2000) Sens Actuators 84:310
8. Kuru Y, Wohlschlogel M, Welzel U, Mittemeijer EJ (2007) Appl Phys Lett 90:24113
9. Kuru Y, Wohlschlogel M, Welzel U, Mittemeijer EJ (2008) Surf Coat Technol 202:2306

10. Suryanarayana C (2001) Prog Mater Sci 46:1
11. Wright RN, Knibloe JR (1990) Acta Metall Mater 38:1993
12. Gialanella S, Delorenzo R, Marino F, Guella M (1995) Intermetallics 3:1
13. Gialanella S, Lutterotti L (1997) Prog Mater Sci 42:125
14. Gialanella S, Delorenzo R, Marino F (1995) Mat Sci Forum 179–181:39
15. Anthony L, Okamoto JK, Fultz B (1993) Phys Rev Lett 70:1128
16. Cahn RW, Takeyama M, Norton JA, Liu CT (1991) J Mater Res 6:57
17. Touloukian YS (1975) Thermal expansion: metallic elements and alloys. Plenum Press, New York
18. Zhao YH, Sheng HW, Lu K (2001) Acta Mater 49:365
19. Qian LH, Wang SC, Zhao YH, Lu K (2002) Acta Mater 50:3425
20. Jang JS, Koch CC (1990) J Mater Res 5:498
21. Lutterotti L, Gialanella S (1998) Acta Mater 46:101
22. Gialanella S, Guella M, Barò MD, Malagelada J, Surinach S (1994) In: de Barbadillo A (ed) Proceedings of the 2nd international conference on structural applications of mechanical alloying, ASM international, Materials Park, Ohio
23. Barò MD, Surinach S, Malagelada J, Clavaguera-Mora MT, Gialanella S, Cahn RW (1993) Acta Metall Mater 41:1065
24. Surinach S, Malagelada J, Barò MD (1993) Mater Sci Eng A168:161
25. Kumpmann A, Günther B, Kunze H-D (1993) Mater Sci Eng A168:165
26. Rupp J, Birringer R (1987) Phys Rev B 36:7888
27. Turi T, Erb U (1995) Mater Sci Eng A204:34
28. Zhu YF, Lian JS, Jiang Q (2009) J Phys Chem C 113:16896
29. Erb U, Palombo G, Szpunar B, Aust KT (1997) Nanostruct Mater 9:261–270