Calorimetric Analyses of Mechanically Alloyed Ni_3Al -Based Powders (*Overview*)

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In this paper, the progress on disordering and the study of the reordering kinetics of nanocrystalline Ni_3Al -based powders prepared by ball-milling were followed by differential scanning calorimetry. A broad exothermic transformation occurs on heating the nanocrystalline Ni_3Al -based powders. The stored energy of cold work has been evaluated by measuring the enthalpy release during heating. The values obtained far exceed the energies achieved by conventional deformation processes. The specific heat increases by more than 5%, indicating changes in vibrational and configurational part of the entropy. The calorimetric analysis of the continuous heating transformation, gives a value for the apparent activation energy of 1.64 ± 0.07 eV, which is very close to the reported values of the activation energies for vacancy migration in these alloys. However, in order to correctly reproduce the calorimetric results obtained upon isothermal annealing, an increasing value for the apparent activation energy of the process is needed. The possible mechanisms involved in the reordering process are discussed.

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I. Introduction

The main driving force for the study and development of advanced alloys and intermetallics is the potential that this class of materials offers as possible high-temperature structural materials for aerospace applications. For this reason, in the last years a considerable amount of work has been done to investigate ordered alloys. In the case of $L1_2(\gamma')$ alloys, they usually undergo a first-order transformation to a disordered fcc(γ) phase when heating beyond a critical transition temperature. The properties of both the ordered- γ' and disordered- γ phases as well as the thermodynamics and kinetics of the order-disorder transformations can be studied by various techniques when the critical transition temperature is below the melting temperature of the alloy⁽¹⁾. However, permanently ordered alloys, like Ni_3Al , have a virtual order-disordered transition temperature above the melting point, and in spite of an inadequate ambient temperature ductility and consequently, a limited workability, this class of materials have a great interest for industrial application due to their high temperature strength, relatively high melting points, and more oxidation and corrosion resistance⁽²⁾⁽³⁾. To improve their mechanical properties, preparation methods are currently being explored that allow the control of microstructural parameters such as lack of atomic order and/or grain size. In particular, powder metallurgical preparation methods are of technological interest and might offer advantages in producing suitable microstructures as compared to conventional ingot metallurgy.

Mechanical milling has been shown to be a versatile powder metallurgical tool for preparing a great variety of structures far from thermodynamic equilibrium⁽⁴⁾⁻⁽⁶⁾. The main aspect involved with ball-milling of metallic powders is the extremely high cold-work energy which can be stored into the materials. It is definitively higher than for any other conventional cold-working technique, such as cold-rolling, tensile and compressive deformations, etc. Depending on materials and experimental parameters, ball milling may typically result in the formation of nanograined powders, showing still crystalline or amorphous structure. Amorphization has been reported in a number of mechanical alloying experiments involving couples of metals with different diffusivities⁽⁷⁾. Likewise several intermetallics has been reported to be prone to amorphization by mechanical milling. Zr_3Al ⁽⁸⁾, Ni_3Ge ⁽⁹⁾⁽¹⁰⁾ just to mention a few recent studies on $L1_2$ phases. In particular, for permanently ordered alloys, like Ni_3Al , mechanical deformation by ball-milling is a very effective tool for obtaining disordered nanocrystalline intermetallic alloys, as found in previous experiments, on this and other $L1_2$ compounds⁽⁶⁾⁽¹¹⁾⁽¹²⁾.

Because of the small crystallite size, these materials consist of two components with comparable volume fraction: a crystalline component comprising all atoms located in the grains and an interfacial component formed by the grain boundaries⁽¹³⁾⁽¹⁴⁾. If the atomic structure of nanocrystalline materials differs from the structures of crystals, the structure-sensitive properties of nanocrystalline materials are expected to be different from those of the chemically identical substances in the crystalline state⁽¹³⁾⁽¹⁵⁾. Since the nanocrystalline structure is a nonequilibrium state and the grains coarsen at ele-

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vated temperatures, the thermal stability is an important subject with respect to possible applications.

In this paper, we report a systematic study to characterize the milling process and to determine the reordering kinetics of disordered nanocrystalline Ni_3Al -based powders prepared by ball-milling using differential scanning calorimetry (DSC).

II. Experimental Methods

As raw material we started from atomized powder (see Table 1), kindly supplied by Knibloe and Wright (Idaho National Engineering Laboratories), who studied the behaviour, with respect to powder metallurgy processing, of these intermetallic powders⁽¹⁶⁾. For the experiments involving $\text{Ni}_{75}\text{Al}_{12}\text{Fe}_{13}$, we started from melt-spun ribbons prepared by Yavari following the procedure described in Ref. (17). The mechanical milling was carried out either in a planetary or a vibratory milling with tempered stainless chrome steels balls and vials. Alternatively, agate vials and yttria-stabilized zirconia balls were used. All experiments were performed under static Ar atmosphere. To study the effect that an inert or reactive atmosphere may have on the disordering kinetics of $\text{Ni}_3\text{Al} + \text{B}$ powders during milling, Ar or H_2 flux was used. The compositions studied as well as the milling conditions are quoted in Table 1. For further details on sample preparation see Refs. (17)–(19).

The integral breadths of the diffraction peaks were used for evaluating the average size of the coherent diffracting domains and the microstrain⁽²⁰⁾. Full experimental procedure regarding X-ray diffraction (XRD) methods can be found elsewhere⁽¹⁸⁾.

The thermal stability of the metastable nanophase formed during ball milling was tested by studying their behaviour on heating in a computerized differential scanning calorimeter (Perkin-Elmer DSC7) under pure Ar atmosphere. Heating was done in an unsealed Au pan using both continuous heating and isothermal regimes. Continuous heating experiments were performed at scan rates in the range 5–160 K/min. The calibration procedure of the apparatus ensures temperature measurements with less than 0.05% error and enthalpy output measurements with a 2% error⁽²¹⁾. The isothermal anneals were carried out in the scanning calorimeter by taking the samples to the annealing temperature at a heating rate of 40 K/min and cooling down at the maximum rate available (~ 200 K/min) down to room temperature after the anneal. The specific heat c_p as a function of temperature was measured and the error in heat capacity measure-

ment was less than 2% using a synthetic sapphire standard for calibration⁽²²⁾.

III. Results and Discussion

1. Metastable nanocrystalline alloys based in L1_2 type structure

As described in previous studies⁽¹⁸⁾⁽¹⁹⁾, mechanical deformation and defects introduced during ball milling progressively reduce the long-range order parameter (LRO). The reduction and further elimination of the LRO is accompanied by progressively refinement of the average crystalline size and increasing of the lattice strain⁽²⁰⁾. It has been proved that, in the early stages of milling, the deformation is localized in dislocation cell structures within shear bands, where the nanometre-size grains nucleate, and that further ball-milling results in an extremely fine grained microstructure with randomly oriented grains separated by large-angle grain boundaries⁽¹³⁾.

On heating the milled samples, reordering, accompanied by grain growth of the crystalline phase from an average initial size below 12 nm, is observed. The results of continuous heating experiences on $\text{Ni}_3\text{Al} + \text{Fe}$ -based powder samples milled for different times are shown in Fig. 1. They reveal the existence of a broad exothermic process where several peaks, which develop on milling are evident. The DSC curves reported in Fig. 2 present a typical result of a continuous heating experiment on some of the nanocrystalline alloys based in the L1_2 type structure studied. Independently of the composition, an exothermic transformation occurs over a wide range of temperatures (373–873 K). Similar DSC curves were obtained in the first work in which the obtention of a disordered nanocrystalline structure in Ni_3Al by mechanical milling is reported⁽²³⁾ and also for Ni_3Al vapour-deposited thin films⁽²⁴⁾. These results suggest that thermal evolution of this compound is not affected by the way in which the metastable disordered nanocrystalline structure is achieved, and indirectly confirm, also for Ni_3Al -based alloys, the analogies between metastable and nanocrystalline structures produced by mechanical attrition and other techniques, such as certain thin-films deposition

Fig. 1 Comparison of DSC curves (40 K/min) from $\text{Ni}_3\text{Al} + \text{Fe}$ -based samples milled for different times: a) 0 h, b) 1 h and c) 2.5 h.

Table 1 Compositions, milling atmosphere and milling media.

Composition	Milling atmosphere	Milling media
$\text{Ni}_{76.6}\text{Al}_{23.3}\text{B}_{0.1}$ ⁽¹⁶⁾⁽¹⁹⁾	H_2 , Ar	Cr-steel, agate
$\text{Ni}_{73.1}\text{Al}_{18.8}\text{Cr}_8\text{B}_{0.1}$ ⁽¹⁶⁾	Ar	Cr-steel
$\text{Ni}_{70.7}\text{Al}_{18.8}\text{Fe}_{10.4}\text{B}_{0.1}$ ⁽¹⁶⁾	Ar	Cr-steel
$\text{Ni}_{75}\text{Al}_{12}\text{Fe}_{13}$ ⁽¹⁷⁾	Ar	Cr-steel

Fig. 2 DSC curves for nanocrystalline complete disordered Ni₃Al-based alloys studied (40 K/min).

Fig. 3 Evolution of DSC curves from Ni₃Al+Fe-based samples milled for 2.5 h as a function of heating rate: a) 10, b) 20, c) 40 and d) 80 K/min.

methods already reported for other systems⁽²⁵⁾.

All these transformations have a kinetic character, easily deduced from their evolution upon heating rate (Fig. 3) and they are irreversible. On repeating a heating DSC scan with the same specimen, no transformation is detected any more. These second scans, performed without changing the sample configuration, were then used as baseline for estimating the total enthalpy output, from the integrated area of the peaks. The evolution of enthalpy released, LRO and average crystalline size as a function of milling time for samples milled in Cr steel media for the Ni₃Al+B specimen are presented in Table 2. The enthalpy release increases with the milling time and even long after long range order has disappeared, no

Table 2 The evolution of enthalpy released Δh (kJ/g.at.), LRO (S/S_0) and average crystalline size ($\langle l_{111} \rangle$) as a function of milling time.

Time (h)	Δh (kJ/g.at.)	S/S_0	$\langle l_{111} \rangle$ (nm)
0.5	1.52	0.72	100
1.0	2.95	0.58	~80
1.5	3.25	0.46	71
2.0	3.46	0.42	~60
2.5	3.74	0.32	55
4.0	5.19	0.18	20
12.0	5.66	0	15
20.0	6.39	0	12

evident steady value is achieved. In this sense, the contribution of grain growth to this enthalpy release cannot be disregarded. According to different authors⁽²⁶⁾⁽²⁷⁾ the enthalpic contribution coming from grain growth in nanocrystalline elemental powders shows values double than that expected for the enthalpy stored in the fully equilibrated grain boundaries of such a refined microstructure. In this case approximately 60% of the enthalpy release can correspond to grain growth. The enthalpy release for a Ni₃Al+B sample milled for 20 h compares well with the value obtained via molecular dynamics simulations of models based on an n-body potential⁽²⁸⁾.

Identification of the processes which may contribute to the complex calorimetric signal has been attempted. For this purpose, isothermal anneals, coupled with further continuous heating experiments which allowed the effect of the anneals to be checked, were performed. In this way, three stages have been identified (Fig. 4), the second, more intense signal being associated with the simultaneous evolution of reordering and grain growth⁽²⁹⁾. This result is again in agreement with those already reported for both milled powders⁽²³⁾ and thin films⁽²⁴⁾. The low-temperature process does not involve any variation in the LRO parameter, as proved by XRD analysis. Harris *et al.*⁽²⁴⁾ regard this peak as determined by reestablishment of short-range order. This hypothesis is nicely proved by the results obtained from electron energy-loss fine structure measurements on Ni₃Al thin films, vapour

Fig. 4 Possible deconvolution of the exothermic process for a Ni₃Al+B sample milled for 20 h.

deposited in the disordered state, and then annealed for several hours at 423 K⁽³⁰⁾. In fact, an excellent agreement was found with the plane-wave calculations used to simulate the environment of each atomic species, when the ordered configuration was adopted. The ordered clusters must necessarily spread only over a few atomic spacings, as no superlattice reflections were detected by conventional X-ray and electron diffraction techniques. A further proof of such attribution of the low temperature peak to short-range reordering is indirectly given by DSC curves reported for elemental milled powders⁽²⁶⁾. They show in fact a complex exothermic process very similar to those we observed for our milled powders. The only substantial difference is the lack of the low temperature peak which, in view of its suggested origin, cannot be present as no chemical reordering can occur in pure metal powders. No clear and conclusive interpretation is proposed for the high temperature, weaker component of the overall transformation. It is also the more difficult phenomenon to deal with, since it strongly overlaps the second process. By considering the temperature range over which it occurs and the low enthalpy associated with it, we infer that it might be due to annealing out dislocations, usually not mobile at temperatures as low as those of the two previous processes.

In order to know the influence of the milling atmosphere, Ni₃Al+B was milled under Ar and H₂. From the XRD results, it is evident that the H₂ atmosphere has a retarding effect on the disordering kinetics, compared to argon and upon milling time they present a different evolution of average crystalline size and lattice strain⁽¹⁹⁾. No significant differences were detected in the DSC curves obtained with the Ar- and H₂-milled samples. In particular no (endothermic) peaks which could be ascribed to gas emission or desorption were found in the analyzed specimens. The only remarkable difference regards the ultimate values of the enthalpy released in the overall exothermic process. They are in fact higher for the powders milled in hydrogen flux and Fig. 5 shows the enthalpy release versus milling time for the Ni₃Al+B based samples milled in agate media under Ar and H₂ atmospheres. The total enthalpy released after 48 h of milling under H₂ atmosphere is higher than a slightly ordered specimen. Our findings seem to agree with⁽²³⁾. We expect in fact the H₂-milled powders to be embrittled by the atmosphere and therefore to be less prone to disordering than those milled in a inert Ar atmosphere. Indeed this is the case, the series of samples prepared under hydrogen flux were still partially ordered for times long enough to completely destroy LRO in the specimens milled under an argon atmosphere. According to⁽³¹⁾ the main reason for hydrogen embrittlement in boron doped Ni₃Al is the stress concentration at grain boundaries which become preferential routes for crack propagation. Several models have been proposed to explain hydrogen embrittlement in terms of grain boundary weakening. With reference to non-hydride forming systems, as Ni₃Al-based alloys are, there are basically two ways in which this phenomenon can occur: either for a decrease in the cohesive strength

Fig. 5 Enthalpy released in the exothermic process as a function of the milling time for Ni₃Al+B samples milled under Ar and H₂ atmosphere using agate media.

of the atomic bonds, or through a localized enhancement of dislocation mobility, near the crack tip, so that slip becomes easier in the nearby regions⁽³²⁾⁽³³⁾. In the light of this model we can argue that, as grain boundaries become preferential sites for slip, lattice defect concentration, due to mechanical milling, increase more slowly inside the grains when hydrogen is used rather than argon. In the light of this considerations and taking into account that the total enthalpy release cannot be ascribed to re-ordering only, but also to the large grain boundary contribution, we can argue that the ultimate value of the average grain size in the H₂ milled powders should be smaller than the final grain size achieved in the Ar-milled powders and it is also possible to explain the slower disordering kinetics observed in the H₂-milled powders, by assuming that a consistent part of the mechanical energy is stored in the material as the grain boundary surface energy.

2. Specific heat

The increase in c_p on going from the original, pre-milled Ni₃Al+B powder to the nanocrystalline state is about 5%. We report a value of $c_p = 25.5$ J/g.at.K at 300 K for the original powder, which presented an average grain size of 100 nm⁽³⁴⁾. Our results agree with the calculated value of 25.7 J/g.at.K by F. Cardellini *et al.*⁽³⁵⁾. An increase of this c_p of 1.1 J/g.at.K at the same temperature for the powder as-milled (in the nanocrystalline state) was found. In Fig. 6 the DSC curve of the sample as-milled relative to the same sample heat-treated at high temperature and, probably, recrystallized is shown. The increase in specific heat at the beginning of the run can be clearly seen.

At room temperature, the equilibrium and even the metastable nanocrystalline Ni₃Al+B, though ground during 42 h in Cr-steel media, are paramagnetic⁽¹⁷⁾. So, the specific heat of the metastable nanocrystalline Ni₃Al alloys, in the temperature range between 300 and 450 K, is due fundamentally to the thermally induced variation

Fig. 6 DSC curve at 40 K/min from a Ni₃Al+B sample milled for 42 h relative to the same sample annealed at high temperature. The increase in specific heat of the as-milled sample is seen as a positive deviation from the zero signal.

of the vibrational and configurational entropy of the materials, the electronic and magnetic contributions being negligible. Taking into account that the vibrational and configurational entropy of the original microcrystalline state and the nanocrystalline structure should be different, an enhancement of c_p for the nanocrystalline Ni₃Al based alloys could be expected, as it was experimentally found. This argument implies that the increase of c_p is principally due to the interfacial disorder. Thus, reordering and grain growth should decrease the specific heat of the metastable nanocrystalline materials to values next to that measured for the original material. In fact, this was observed when the metastable nanocrystalline Ni₃Al based alloys were annealed in the DSC at 950 K to produce reordering and grain growth, being the grain size after the annealing about 40 nm, and the c_p value found for such annealed alloy is 0.5 J/g.at.K larger than that obtained for the microcrystalline material. Our results significantly agree with those recently reported for pure metals and intermetallic phases⁽³⁶⁾⁽³⁷⁾ and also for nanocrystalline materials obtained from crystallization of amorphous Ni-P alloys⁽³⁸⁾.

3. Reordering kinetics

Kinetic analysis based on calorimetric measurements has been performed on the second contribution to the exothermic peak of a Ni₃Al+B-based sample which was milled for 20 h in Cr steel media. As stated before, this contribution is associated with reordering and grain growth⁽²⁹⁾.

The peak method⁽³⁹⁾ was used to evaluate the apparent activation energy, E . The A value of $E=1.64\pm0.21$ eV was found for a Ni₃Al+B-based sample milled for 20 h. The values of E obtained in this way for the reordering and grain growth process, remain constant irrespective of the milling time, within the experimental errors⁽¹⁸⁾. The value found agree with the apparent activation energy for reordering of Ni₃Al in⁽²³⁾⁽⁴⁰⁾. It is significant that this value is in good agreement with those deduced from XRD results for reordering ($E=1.57\pm0.20$ eV) and ordered

domain growth ($E=1.61\pm0.07$ eV). The coincidence of the apparent activation energy for reordering and ordered domain growth seems to indicate that reordering occurs through the formation and coarsening of ordered domains⁽²⁹⁾. We find in fact that the apparent activation energy as measured using different techniques is in rough agreement with the energy of vacancy migration in Ni₃Al, as measured by positron annihilation experiments: 1.2 ± 0.2 eV⁽⁴¹⁾. Similar values of E have been obtained for all the samples analyzed, irrespective of their compositions⁽⁴²⁾⁽⁴³⁾.

As well as in continuous heating regime, calorimetric results have been obtained by operating the DSC in isothermal regime. This is a usual procedure to extend the temperature range available to calorimetric measurements and thus to increase the precision in kinetic analysis⁽²¹⁾. The isothermal DSC curves obtained at two different temperatures after heating from room temperature at a scanning rate of 40 K/min are shown in Fig. 7. Two facts, however prevented us from getting all the information expected from these isothermal regime measurements. First, the signal is characterized by a continuous decay. Second, at temperatures which correspond to early stages of the contribution studied, and even after long annealing times (several hours), the process has not gone to completion, as evidenced on further continuous heating. For these reasons a deeper understanding of the reordering kinetics can be achieved by coupling isothermal with further continuous heating experiments.

The kinetic analysis of the transformation process has been done in terms of the transition state rate theory, which properly describes the kinetics of many thermally activated solid-state reactions. For this purpose, the fraction transformed, α , and its rate, $d\alpha/dt$, have been determined for the different experiments. It has been assumed that the rate of heat generated during the exothermic process studied is proportional to the transformation rate, $d\alpha/dt$. Therefore, the fraction transformed, α , at a time, t , is determined as a ratio between the partial area under DSC curve at that time and the total area of the exothermic peak⁽⁴⁴⁾.

Many studies have shown⁽⁴⁵⁾ that continuous heating experiments allow a good kinetic description to be obtained

Fig. 7 Isothermal DSC curves from a Ni₃Al+B-based sample milled for 20 h.

by assuming that the rate of transformation is given by

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where $k(T)$ is the reaction rate, generally given by an Arrhenius expression

$$k(T) = k_0 \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where E is the apparent activation energy and k_0 the pre-exponential factor both independent of temperature or progress of the transformation provided that the temperature range over which the transformation occurs is not too wide. In the classical nucleation-and-growth process, as depicted by the Johnson-Mehl-Avrami-Erofe'ev (JMAE) analysis⁽⁴⁶⁾, the function $f(\alpha)$ is given by the expression

$$f(\alpha) = p(1-\alpha)[- \ln(1-\alpha)]^{(p-1)/p} \quad (3)$$

where p is the kinetic exponent that, depending on the nucleation mechanism and growth morphology, varies between 0.5 and 4⁽⁴⁷⁾. Assuming $E = 1.64 \pm 0.21$ eV, the other parameters have been determined by fitting the simulated calorimetric DSC signal that can be deduced from the model to the experimental DSC signal of the reordering process of the sample studied. The results obtained were $k_0 = 3.10^{10}$ and $p = 0.6$ ⁽⁴⁸⁾. As it is well known, the value of $p = 0.6$ in the JMAE model can correspond to a one- or two-dimensional growth of ordered regions, diffusion-controlled from the pre-existing ordered nuclei, the ordered regions consuming the surrounding disordered material until the regions impinge at antiphase domain boundaries. Similar kinetic parameters were evaluated for the reordering kinetics of $\text{Ni}_3\text{Al} + \text{Fe}$ -based alloys from magnetic measurements⁽⁴⁹⁾.

As commented above, isothermal measurements can increase the precision in kinetic analysis. However, the fact that the calorimetric signal decreases from the very beginning of the transformation prevents one from getting better accuracy through the isothermal rate of transformation. Kinetic data available from isothermal measurements can only be evaluated from continuous heating experiments performed before and after the anneals. Only in this way it is possible to know the extent at which the transformation has proceeded during the anneal⁽⁵⁰⁾. The anneals performed complete the transformation progressively, as shown in Table 3 and Fig. 8 upper figure. The simulation of the continuous heating curves shown in

Table 3 Transformed fraction (α_{iso}) obtained at different annealing temperatures during different times.

t (h)	α_{iso} at		
	473 K	523 K	573 K
1	0.06	0.23	0.68
3	0.08	0.37	0.81
10	0.13	0.51	0.88
25.5		0.62

Fig. 8 Upper figure continuous heating curves at 40 K/min obtained after isothermal anneals at 523 K during: a) 0, b) 1, c) 3, d) 10 and e) 25.5 h on one of the samples analysed. The third contribution is subtracted and only the second contribution to the DSC peak is shown. Lower figure simulation of the continuous heating curves shown in upper figure according to the JMAE model. The following parameters have been used: $E = 1.64$ eV, $k_0 = 3.10^{10}$ and $p = 0.6$.

Fig. 8 upper according to the JMAE analysis are presented in Fig. 8 lower figure. The JMAE analysis fails to reproduce the calorimetric results observed upon isothermal annealing.

To determine why the JMAE analysis was not able to reproduce the calorimetric behaviour after isothermal anneals, we have developed an empirical description where the function $k_0f(\alpha)$ has been evaluated from the experimental data ($d\alpha/dt$, α , T) by combining eqs. (1) and (2)⁽⁵¹⁾. According to this empirical description, the values which give the best fit to the experimental data are $E = 1.64 \pm 0.21$ eV and $k_0f(\alpha)$, as plotted in Fig. 9. It is worth noting that the empirical function used here has been deduced from a continuous heating run under specific conditions; however, its correct reproducibility has been checked with reference to different conditions (see Fig. 9).

In order to reproduce the rate of fraction transformed from this description, knowledge of the relationship between temperature or time and the fraction transformed is needed. For this purpose the function $g(\alpha)$ is introduced. According to current usage, the following definition is used:

Fig. 9 Plot of the function $k_0 f(\alpha)$ vs α . Dashed lines are obtained from the DSC signal, corresponding to the second exothermic event, for 40 and 80 K/min. Solid line corresponds to the best fit to experimental results. $E=1.64$ eV.

Fig. 10 Simulations of the calorimetric signal according to the empirical description given by equations (1) and (2) (dashed lines) compared to the experimental one (solid line) for heating rates a) 20, b) 40 and c) 80 K/min. $E=1.64$ eV.

$$\frac{g(\alpha)}{k_0} = \int_0^\alpha \frac{d\alpha}{k_0 f(\alpha)} \quad (4)$$

which can be put, using (1) and (2), as

$$\frac{g(\alpha)}{k_0} = \frac{1}{\beta} \int_0^T \exp\left(-\frac{E}{RT'}\right) dT' \quad (5)$$

for continuous heating regime, at rate β , or

$$\frac{g(\alpha)}{k_0} = t \exp\left(-\frac{E}{RT}\right) \quad (6)$$

for isothermal regime. Once the relationship between α and T is obtained, the rate of fraction transformed is deduced. The results are compared to the experimental data in Fig. 10 for different values of the heating rate.

To analyse the behaviour observed after coupled isothermal and continuous heating treatment, eq. (4) can be developed to obtain the fraction transformed after a series of thermal treatments on the same specimen from

$$\frac{g(\alpha)}{k_0} = \int_0^{\alpha_1} \frac{d\alpha}{k_0 f(\alpha)} + \int_{\alpha_1}^{\alpha_2} \frac{d\alpha}{k_0 f(\alpha)} + \dots + \int_{\alpha_{n-1}}^{\alpha_n} \frac{d\alpha}{k_0 f(\alpha)} + \int_{\alpha_n}^{\alpha} \frac{d\alpha}{k_0 f(\alpha)} \quad (7)$$

where each term of the right member of this equation is explicitly calculated using eqs. (5) or (6) corresponding to the specific thermal treatment which induces progressive completion of the process up to a fraction transformed, α .

For the values of α in the range 0.2–0.4, the use of an apparent activation energy of $E=1.64$ eV allows an accurate reproduction, not only of the fraction transformed but also on its further evolution under continuous heating, as shown in Fig. 11 upper but the use of the same E fails to reproduce the experimental behaviour observed after an isothermal anneal at 523 K during 25.5 h ($\alpha=0.62$) Fig. 11 down. The discrepancy between the simulated and the experimental curves may be due to the approximate description of $k(T)$ given by eq. (2) and strongly suggests that the apparent activation energy changes not only with T but with α .

Figure 12 shows the values of $g(\alpha)/k_0$ obtained from continuous heating experiments and the corresponding discrete values of the same quantity obtained from isothermal measurements for different values of the apparent activation energy. As presented in Fig. 13 and

Fig. 11 Simulation (dashed line) of the behaviour observed on further continuous heating after an isothermal anneal at 523 K during 1 h (upper figure) and 523 K for 25.5 h (lower figure) together with the experimental result (solid line). Heating rate 40 K/min; $E=1.64$ eV.

Fig. 12 Plot of the function $g(\alpha)/k_0$ vs α deduced from continuous heating measurements using different E values (solid line) together with the discrete values of the same function obtained from isothermal anneals (filled squares).

Fig. 13 Simulation of the behaviour observed on further continuous heating after an isothermal anneal at 523 K during 25.5 h (dashed line) together with the experimental result (solid line). Heating rate 40 K/min; $E = 1.85$ eV.

when $\alpha \geq 0.5$, a value of $E = 1.85$ eV is needed to reproduce the experimental results.

The increase which is observed in the values of the apparent activation energy with T and α cannot, in this case, be attributed to reordering. It is well known that the activation energy for diffusion in B2 ordering is higher in the ordered domain than in the disordered domain⁽⁵²⁾. However, there is no direct evidence of difference in these values for the ordered and disordered alloy on L1₂ ordering, which implies that neither the formation nor the migration energies for vacancies are affected by the degree of order⁽⁵³⁾. A possible explanation comes then from the following considerations:

(a) Mechanical milling induces a substantial quantity

of excess point defects. The concentration of excess point defects is assumed to control the kinetics of reordering, in which case the measured activation energies can be related to vacancy migration. In previous work by the authors⁽⁴¹⁾⁽⁴²⁾ and by others, either on Ni₃Al disordered by cold-working⁽⁵⁴⁾⁽⁵⁵⁾ or by irradiation⁽⁵⁶⁾, good agreement was found between the measured activation energies and the energy for vacancy migration in Ni₃Al.

(b) This high concentration of excess point defects, mainly vacancies and antisites⁽⁵⁷⁾⁽⁵⁸⁾, assists diffusive processes and tends to be eliminated upon annealing. However, there is still a substantial fraction of the material remaining in the disordered state even after a long-term anneals, which indicates that defects are still present and prevent the completion of the recovery process⁽⁵⁰⁾.

(c) Contamination of the Ni₃Al powders during the milling process is unavoidable. Some of the contamination occurs in solution and the increase in the Curie temperature of the samples which were milled using tempered chromium-steel balls and vials, due to the presence of Fe in solution⁽¹¹⁾⁽⁴⁹⁾, is an example of this. The grinding impurities (in solid solution) can act as obstacles to defect migration, affecting in this way the observed kinetics.

In view of these observations we consider the model proposed in⁽⁵⁹⁾ for vacancy annealing in impure metals. In the case of a low concentration of defects and impurities, an apparent activation energy for migration of vacancies, E_e , is found and it depends both on temperature and on the total impurity concentration x_1^0 . Specifically

$$E_e = E_m + \frac{k_1^0 e^{B/(RT)} x_1^0 B}{1 + k_1^0 e^{B/(RT)} x_1^0}, \quad (8)$$

E_m being the vacancy migration energy in the solvent, k_1^0 being of the order of unity and B being a vacancy-impurity binding energy. Typical values for B fall within the range 0.2–0.5 eV⁽⁵⁹⁾⁽⁶⁰⁾. The presence of impurities may explain the kinetic results if their total concentration, x_1^0 , progressively increased. This could be accounted for through the reduction in the volume occupied by the disordered matrix (which would contain the defects and impurities) during ordering.

IV. Conclusions

The progress on disordering and the study of the reordering kinetics of disordered nanocrystalline Ni₃Al-based powders prepared by ball-milling were followed by differential scanning calorimetry.

The differential scanning calorimetry experiments show that, when heating disordered nanocrystalline Ni₃Al alloys, a broad exothermic transformation occurs. The deconvolution of the complex calorimetric signal reveals three stages, the second being associated with the simultaneous evolution of reordering and grain growth.

The enthalpy released during the heating of disordered nanocrystalline Ni₃Al-based alloys has been measured. The values obtained far exceed the energies achieved by

conventional deformation processes. The total enthalpy released in the process indicates that the main contribution was associated to grain growth and the rest to chemical reordering. No significant differences were detected in the DSC curves obtained with the Ar- and H₂-milled samples. In particular no (endothermic) peaks which could be ascribed to gas emission or desorption were found in the analyzed specimens. The only remarkable difference regards the ultimate values of the enthalpy released in the overall exothermic process. They are in fact higher for the powders milled in hydrogen flux.

Specific heat measurements in the temperature range between 300 and 450 K revealed that the c_p of the disordered nanocrystalline Ni₃Al alloys were about 5% higher than in the microcrystalline state. The enhancement of c_p in this disordered nanocrystalline Ni₃Al alloys might be attributed to changes in vibrational and configurational part of the entropy, probably due to the complicated structure of the grain boundaries.

The calorimetric analysis of the continuous heating transformation, gives a value for the apparent activation energy of 1.64 ± 0.07 eV. It is significant that this value is in good agreement with those deduced from XRD results for reordering ($E = 1.57 \pm 0.20$ eV) and ordered domain growth ($E = 1.61 \pm 0.07$ eV). The coincidence of the apparent activation energy for reordering and ordered domain growth seems to indicate that reordering occurs through the formation and coarsening of ordered domains. We find in fact that the apparent activation energy as measured using different techniques is in rough agreement with the energy of vacancy migration in these alloys. Similar values of E have been obtained for all the samples analyzed, irrespective of their composition.

However, the calorimetric results are in fact best fitted if an activation energy continuously varying with the fraction of the transformed phase is assumed. This increase of the apparent activation energy with the degree of transformation cannot be attributed to ordering. A possible explanation is that the impurities present in the samples coming from the grinding media, affect the observed kinetics.

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