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Influence of plastic deformation on occurrence of discontinuous precipitation reaction in Ni-3 at% In alloy

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ABSTRACT

This present study is an attempt to investigate the plastic deformation effect on development of discontinuous precipitation reaction in Ni-3 at% In alloy by applying three different pre-reduced samples by cold rolling (ε=10%, 30% and 60%). Differential scanning calorimetry (DSC), X-ray diffraction, optical microscopy and microhardness measurements were used as techniques of characterization. We have found that the occurrence of this reaction depends mainly on the deformation ratio before heat treatments. The variation of heating rate using the DSC technique has allowed us to calculate two kinetics parameters of precipitation, which are the Avrami exponent and the activation energy of the process.

1. Introduction

Discontinuous precipitation represents a solid-state reaction in which a supersaturated solid solution is replaced by two-phase structure. From both scientific and industrial viewpoints, this reaction has been of great interest for a long time. This interest is not only in the reaction mechanism itself but also in the enormous material property changes it can cause [1–3]. In Ni–In alloys the discontinuous precipitation reaction has been observed by several investigators [4–7]. This reaction is characterized by the growth of two lamellar phases from grain boudaries in a supersaturated solid solution (α_0). These lamellae are a precipitate β (Ni_3In of DO_{19} structure) and the depleted matrix (α), which is a Ni rich solid solution of CFC structure.

However, it has been reported that prior deformation enhances this discontinuous precipitation kinetics in some alloys such as Cu–In [8], Ni-based superalloys [9], Pb–Na [10] and Nb–Zr–Ti [11]. The opposite effect has been observed in Cu–Be [12], Cu–Ni–Mn [13] and Al–Li [14]. For this last case, a high matrix dislocation density as a consequence of prior straining may enhance continuous precipitation and thereby reduce the driving force for discontinuous precipitation [15]. Among these cases, some studies have shown that the mode of deformation can determine whether discontinuous precipitation kinetics is enhanced or decreased [16]. For the other cases, the rate of plastic deformation can also have an effect on discontinuous precipitation occurrence. For example, according to Bohm [17], as far as the 10–20% deformation Cu–In alloys are concerned, the cell's growth rate increases at the beginning of the discontinuous precipitation reaction. For 50% deformation, it slows down earlier. Williams and Butler [14] asserted that under the influence of plastic deformation the kinetics of the continuous precipitation increases.

We notice that this present investigation of Ni-3 at% In alloy is a new contribution to our recent study of the plastic deformation effect on the occurrence of discontinuous precipitation in Al–Zn [18]. In addition, different kinetics parameters are calculated for Ni-3 at% In alloy by applying the theory of Avrami [19] and Johnson and Mehl [20], which is based on the transformed volume fraction of the precipitated product that is nucleated at grain boundaries, during the ageing time under non-isothermal condition. Contrary to the previous research studies about a discontinuous precipitation in binary alloys, our material is submitted to a non-isothermal treatment in order to develop a discontinuous precipitation.

2. Experimental procedures

The Ni-3 at% In alloy was prepared by the use of high purity nickel and indium (99.99%), which are melted in a vacuum of 1.5 mPa (10^{-5} Torr). The ingots were homogenized in vacuum at 1000 °C for 20 h and quenched in water so as to obtain a supersaturated solid solution α_0. For differential scanning calorimetry (DSC) analysis, some

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disks of 3 mm diameter and 1 mm thickness were used. The DSC measurements were performed with a NETZSCH 200 PC DSC. To prevent oxidation of the samples during different analyses by DSC, a protective atmosphere of nitrogen was used. X-ray diffraction analysis is performed by PANalytical X' Pert PRO diffractometer using CuK_{α} radiation, scanned at a speed of 0.9°/min. For microscopic studies, specimens were chemically etched with a concentrated solution of 10% $FeCl_3$ in ethanol at room temperature for 30–90 s.

3. Results and discussion

3.1. DSC analysis

In order to study, by DSC, the plastic deformation effect on the kinetics of discontinuous precipitation, the samples are homogenized at 1000 °C for 20 h, and water quenched followed by a cold plastic deformation with different rates of deformation $\varepsilon=10\%$, 30% and 60% of reduction. These samples are submitted to non-isothermal treatment by DSC between 50 and 500 °C (Fig. 1). These DSC curves show an exothermal peak that corresponds to heat emission along discontinuous precipitation. The different shapes of peaks indicate clearly that the kinetics of discontinuous precipitation is influenced by the rate of plastic deformation.

The transformed fraction Y, which characterizes the running rate of the reaction at a corresponding T_j temperature, is given by the formula $Y=\Delta S_j/S=\Delta H_j/\Delta H$, where S is the total surface of the exothermic peak, S_j the partial surface at this temperature, ΔH the total enthalpy of the reaction and ΔH_j the partial enthalpy at this temperature.

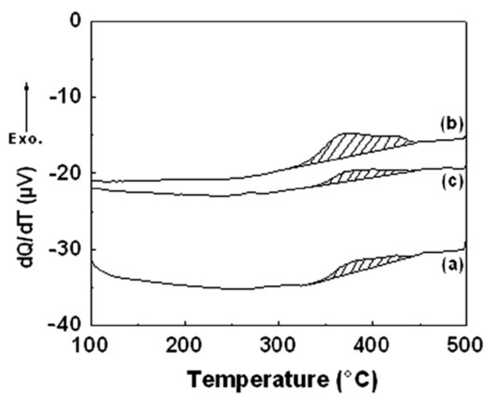

Fig. 1. DSC curves of Ni-3 %at In alloy homogenized for 20 h at 1000 °C, quenched and deformed at $\varepsilon=10\%$, 30% and 60% of reduction (heating rate $\alpha=15$ °C/min).

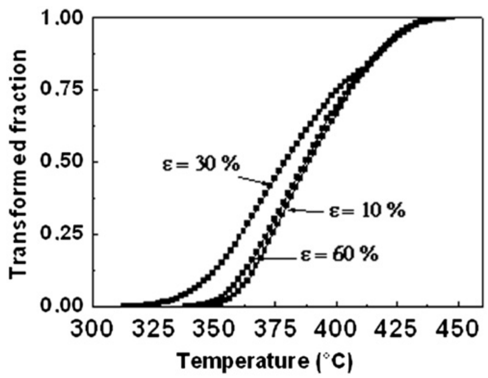

Fig. 2. Transformed fraction of Ni-3 %at. In alloy as a function of temperature.

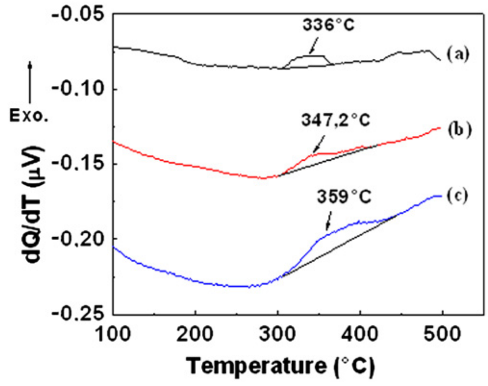

Fig. 3. DSC thermograms of Ni-3 at% In alloy as a function of heating rate α: (a) $\alpha=2$ °C/min, (b) $\alpha=4$ °C/min and (c) $\alpha=6$ °C/min .

On the other hand, investigation of the peaks in Fig. 1 enables us to plot the evolution of transformed fraction Y with temperature for different deformations (Fig. 2). This figure shows the influence of deformation rate on the kinetics of discontinuous precipitation. We have noticed that the increase in deformation rate (10% and 30%) leads to a displacement of the transformation curve towards the left. This displacement represents an advance of the reaction of discontinuous precipitation. However for a 60% rate we note a shift towards the right.

In order to study the behavior of Ni-3 at% In alloy during heating or cooling, differential calorimetric analysis (DSC) remains one of the best techniques for the detection of the phase transformations in a solid state and measurement of its energy.

Fig. 3 presents the DSC curves recorded for the samples at different heating rates ($\alpha=2$, 4 and 6 °C/min). These curves show an exothermic peak, which corresponds to the release of energy during discontinuous precipitation. It is noticed that the top of the peak moves towards high temperatures when the heating rate increases.

4. Calculation of activation energy

To determine the activation energy, the methods of Kissinger [21], Ozawa [22] and Boswell [23] are used. These methods determine the activation energy of a system starting from the change in the temperature that corresponds to the maximum of the exothermic peak T_m according to the heating rate α.

$$Y=\ln\left(\frac{\alpha}{T_m^2}\right)=-\frac{E}{RT_m}+C \quad \text{Kissinger equation}$$

$$Y=\ln\alpha=-1.0518\frac{E}{RT_m}+C_1 \quad \text{Ozawa equation}$$

$$Y=\ln\left(\frac{\alpha}{T_m}\right)=-\frac{E}{RT_m}+C_2 \quad \text{Boswell equation}$$

Note that, C, C_1 and C_2 are constants, E is the activation energy (J/mole) and R the perfect gas constant (8.314 J/mole K)

The activation energies deduced from the curve's slopes of Fig. 4 are very close and these values are in accordance with the literature [24,25]. The results are included in Table 1, which represents the activation energy that is determined by three methods for the Ni 3%at In alloy, which has been quenched and heated from 25 to 500 °C at different heating rates $\alpha=2$, 4 and 6 °C/min.

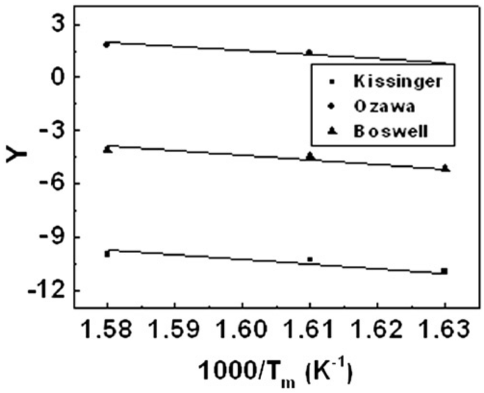

Fig. 4. $Y=f\,(1000/T_m)$ curves of Ni-3 at% In alloy using three different methods.

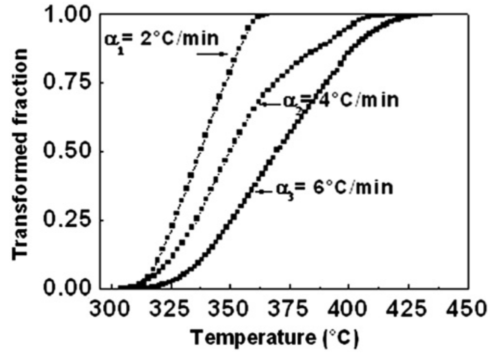

Fig. 5. Transformed fraction of Ni-3 at% In alloy at different heating rates α=2, 4 and 6 °C/min as a function of temperature.

Table 1

Method	Kissinger	Ozawa	Boswell
Activation energy (kJ mol^{-1})	214.97	205.51	223.29

5. Avrami index calculation (n)

The curves obtained from Fig. 5 are S-shaped curves or sigmoïdal, showing the transformed fraction according to the temperature for various heating rates. It is noticed that the increased heating rate leads to a shift of the exothermic peaks towards greater temperatures.

To calculate the coefficient n (Avrami index), a characteristic of the transformation mechanism that controls discontinuous precipitation in Ni-3 at% In alloy, we used the equation of Matusita et al. [26], which connects the fraction that transformed Y to a constant temperature and the heating rate according to the following equation:

$$\ln[-\ln(1-Y)] = -n\ln\alpha + C$$

The plotted curves corresponding to the function $\ln[\ln(1-Y)^{-1}]=f(\ln\alpha)$ are presented in Fig. 6 at two temperatures (T_j=350 °C and $T_{j'}$=360 °C). Two straight lines are obtained with a slope n=1.79 for 350 °C and n=1.88 for 360 °C. The mean value of n Avrami coefficient is 1.83, which may correspond to a phase transformation mechanism driven by diffusion. These values are in agreement with works on Ni–In alloy, in which the values lie between 1.54 and 1.96 for temperatures ranging from 438 to 680 °C [24,27].

To study the effect of the treatment of non-isothermal DSC on the kinetics of discontinuous precipitation in Ni-3 at% In alloy, homogenized at 1000 °C during 20 h, water quenched and deformed at 10%, 30% and 60%, the whole samples were passed directly to DSC (heated from 30 to 500 °C at the heating rate α=15 °C/min).

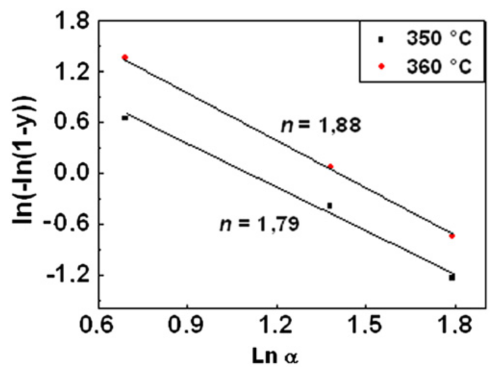

Fig. 6. $\ln(\ln(1-Y)^{-1})=f(\ln\alpha)$ curves of Ni-3 at% In alloy at two different temperatures.

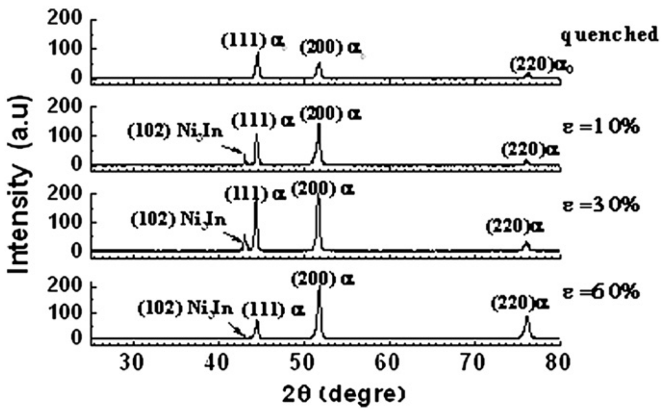

Fig. 7. X-ray spectra diffraction of Ni-3 at% In alloy quenched and deformed 10%, 30% and 60% (after DSC treatment).

5.1. X-ray diffraction analysis

X-ray diffraction spectra of these samples that have been carried out after DSC are shown in Fig. 7. This technique reveals interesting information about the effect of plastic deformation on the kinetics of discontinuous precipitation.

The first deduction is that kinetics of the discontinuous precipitation reaction is fast and the intermetallic phase θ(Ni_3In) corresponds to the equilibrium diagram and agrees with the data in the literature[5,8,28].

It is clear that intensity of the (102) peak corresponds to that of the precipitate (Ni_3In). The peak intensity increases from 38.10 to 62.07 a.u. with the deformation rate increasing from 10% to 30% of reduction, but this intensity decreases in the case of 60% of reduction, which reveals a lack (absence) of discontinuous precipitation.

5.2. Microstructural analysis

Fig. 8 illustrates the microstructures of the aged Ni-3 at% In alloy, homogenized at 1000 °C for 20 h, quenched in water, and deformed at 10%, 30% and 60%.

It is clear that discontinuous precipitation occurs only for prior cold working at 10% and 30% of reduction (Fig. 8b and c), but it is missing for highly deformed alloy (60%). The development of discontinuous precipitation for low deformation is due to the

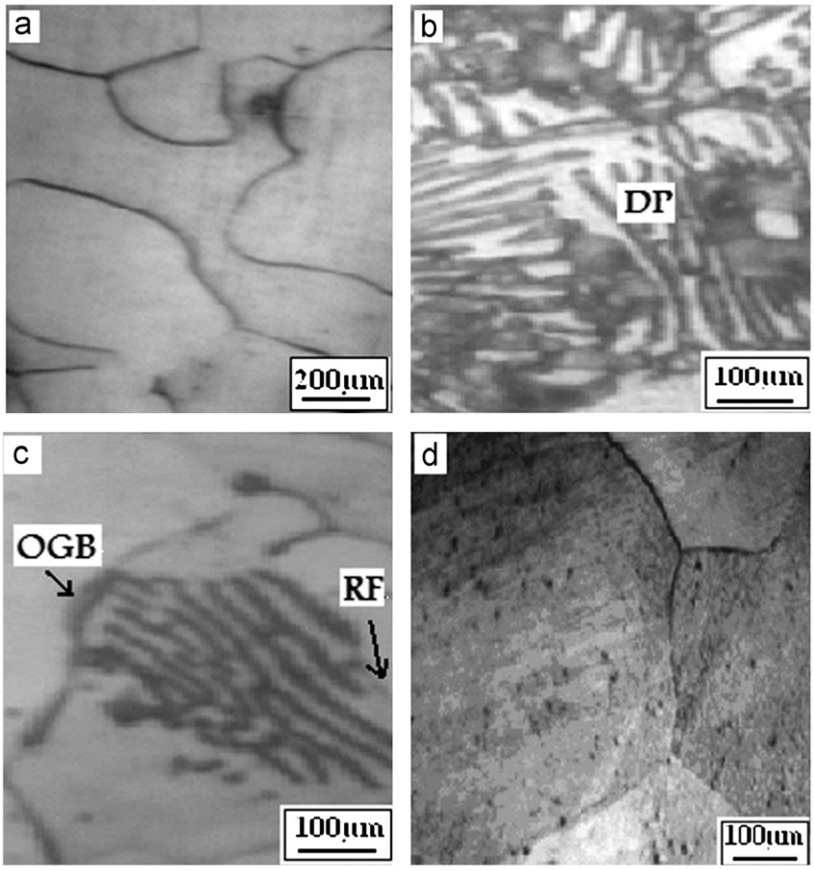

Fig. 8. Microstructures of Ni-3 at% In alloy homogenized at 1000 °C for 20 h; quenched and deformed 10% (a), 30% (b, c) and 60% (d), OGB—original grain boundary, RF—reaction front, and DP—discontinuous precipitation (microstructures after DSC treatment).

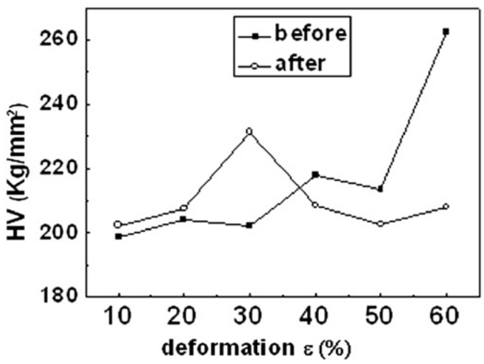

Fig. 9. Evolution of microhardness as a function of plastic deformation in Ni-3 at% In alloy (before and after DSC treatment).

contribution of the energy of the deformation, which is stored in the matrix after cold rolling. These observations confirm the result obtained by X-ray diffraction.

5.3. Microhardness analysis

Fig. 9 shows the HV microhardness of Ni-3 at% In alloy as a function of deformation (before and after DSC treatment of deformed samples from 25 to 500 °C, $\alpha = 15$ °C/min).

The curve (a) reflects the phenomenon of hardening by plastic deformation. However, the curve (b) obtained after DSC tests shows that the maximum Vickers hardness corresponds to 30% reduction, which corresponds to the formation of an important quantity of θ(Ni_3In) precipitate (Fig. 9).

6. Conclusion

The occurrence of discontinuous precipitation in predeformed Ni-3 at% In alloy has been studied. We have found that this reaction is stimulated by prior cold rolling before anisothermal treatments, but below the critical deformation, which is 30% of reduction. The maximum hardness corresponds to the formation of an important quantity of θ(Ni_3In) precipitate particles at this ratio of reduction. Moreover, the activation energy of discontinuous precipitation is calculated ($E = 214.59 \pm 8.7$ K J mol^{-1}) and the n Avrami coefficient that characterizes the transformation mechanism, controlling the discontinuous precipitation in Ni-3 at% In alloy, is determined ($n = 1.83$).

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