GLOBAL JOURNAL OF PURE AND APPLIED SCIENCES VOL. 10, NO. 1, JANUARY 2004: 101-110
 ISSN 1118-0579

EFFECT OF COOLING RATES ON THE MICROSTRUCTURE AND CRYSTALLOGRAPHIC PROPERTIES OF Ni-Ni_3B EUTECTIC

JOHN A. AJAO and SYLVAINE HAMAR-THIBAULT

(Received 26 May, 2003; Revision accepted 24 July, 2003)

ABSTRACT

The crystallographic and microstructural properties of the binary lamellar Ni – Ni_3B eutectic prepared under various cooling rates had been investigated using differential thermal analysis (DTA), scanning electron microscopy (SEM), X-ray diffraction (XRD) and transmission electron microscopy (TEM). It was observed that for low cooling rates, the theoretical law "λ^2V = constant" was valid. However, for high solidification rates (meltspinning), the interlamellar spacing (λ) seemed independent of the cooling rate. Crystallographic orientation relationships between the two phases of the eutectic under three cooling conditions were proposed. In the DTA mode (slow cooling), the relationship between the two phases was stable. However as the cooling rates increased (quenching and meltspun modes), the relationship tended towards metastability.

KEYWORDS: alloy, solidification, microstructure, eutectic, volume fraction.

1. INTRODUCTION

The enhancement of mechanical properties of Ni-B alloys increases with boron content has been reported by Campbell et al (1988). The high hardness value of these alloys suggests their application as wear-resistant coatings under various working conditions (Knotek et al 1974, Ajao et al 1995). It has also been demonstrated that the wear resistance of Ni-B alloys increases with boron content and is excellent for alloys containing 13.0 and 37.0 at %B in pin-on-disc experiments where the pin was glass-filled epoxy (Campbell et al 1988). The equilibrium solid solubility of boron in nickel is quite low, with a maximum of the order of 0.3% at the Ni – Ni_3B eutectic temperature of 1093^{0}C. A large amount of undercooling has been reported during slow cooling of these alloys (Ajao et al 1988) which has been explained by difficulty of the Ni_3B phase to nucleate from the melt. The binary Ni – Ni_3B eutectic is common ir these coating alloys. The eutectic

JOHN A. AJAO, Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Nigeria.
SYLVAINE HAMAR-THIBAULT, INPG-ENSEEG, LTPCM (CNRS), URA), BP 75, 38402 Saint Martin D'Heres, Cedex, France.

composition is Ni - 16.2%B (Ajao et al 1988).

Since this eutectic composition falls within the range of composition of wear resistant industrial application of these alloys and is common in these wear resistant coatings, its microstructural and crystallographic characteristics under various cooling conditions needs extensive investigation. This article describes the investigation on the crystallographic behaviour as well as the microstructure of the binary Ni-Ni_3B eutectic subjected to a wide range of cooling rates from slow cooling in differential thermal analysis (DTA) to quenching by meltspinning technique.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of the eutectic alloy.

The eutectic composition was prepared from pure Ni and NiB containing 15%B. Accurately weighed components of the alloy were arc-melted in an argon atmosphere using a non-consumable tungsten electrode. This operation was repeated several times to ensure the homogenization of the sample.

2.1.1 DTA samples

The melting behaviour and phase formation were determined by differential thermal analysis (DTA) in a semi-quantitative automatic apparatus at LTPCM, Grenoble, France (Ajao 1988). This apparatus allows the automatic control of thermal programs and automatic analysis of the results. The heating and cooling rate is 5^0C min^{-1}.

2.1.2 Quenched from the liquids samples

During heating in DTA, some samples were quenched in air from the liquidus. The cooling rate in this case has been estimated at $10^0C\ s^{-1}$ (Ajao 1988).

2.1.3 Meltspun samples

Some samples were produced by the meltspinning technique (developed at LTPCM, Grenoble, France) which consists of induction-melting the accurately weighed mixtures of pure metal (nickel) and nickel boride (NiB) of eutectic composition in a crucible with a nozzle (diameter = 0.8mm) through which the molten alloy is ejected on to a cooled rotating copper surface under an ambient pressure of about 200mbar helium. The temperature of the liquid alloy before ejection onto the rotating copper wheel was kept at about 50^0C above the eutectic temperature. The wheel surface velocity used in this work varied from 15 to $45ms^{-1}$. The ribbon alloy produced were 1 to 2mm wide and 30 to 50µm thick. The cooling rate was estimated between 2 and $5x10^5Ks^{-1}$.

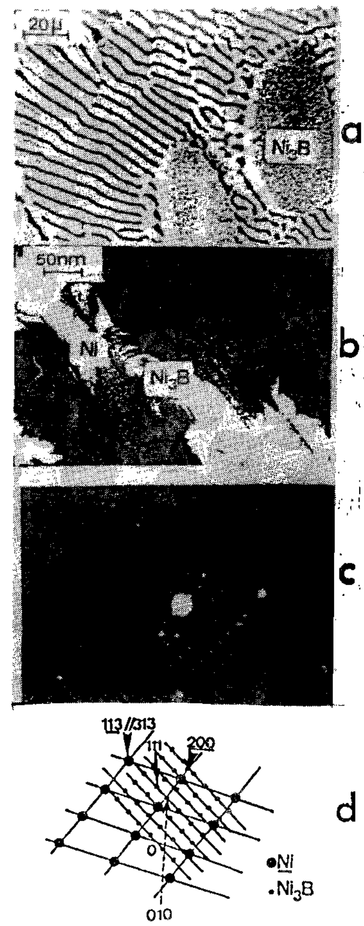

Figure 1:(a) SEM of the Ni-Ni$_3$B eutectic after DTA ($5^oC/min^{-1}$)

(b) Microstructure of the eutectic on TEM

(c) Superposed diffraction pattern

(d) Key diagram

2.2 Sample characterization

The microstructure of the alloy and the nature of the phases were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM - JSM35) equipped with energy dispersive X-ray analysis system (EDXA - TRACOR) and transmission electron microscopy (TEM) performed on thin foils. The samples for SEM observations were slightly etched with an etchant consisting of 5g $FeCl_3$ + 10ml Conc HCl dissolved

in 50ml H_2O. Thin foils were obtained by electropolishing using electrolyte containing 57% H_2SO_4 in H_2O at room temperature under 10V.

3.0 EXPERIMENTAL RESULTS

3.1 Morphology of the Ni-Ni$_3$B eutectic

The microstructure of the binary Ni-Ni$_3$B eutectic observed in the three modes of

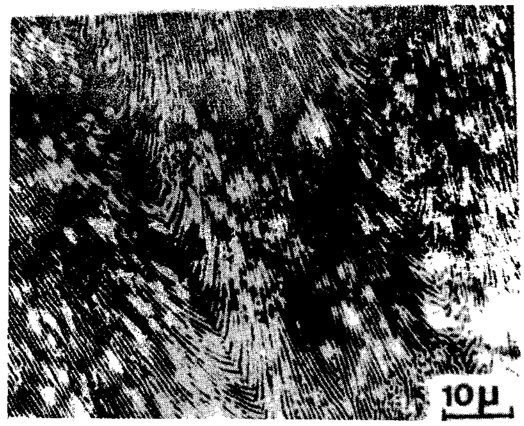

Figure 2: SEM of the Ni - Ni_3B eutectic quenched from the liquidus.

cooling is lamellar but with varied interlamellar spacings. Figure 1a and b respectively show the scanning electron micrograph and transmission electron micrograph of the slowly cooled Ni-Ni_3B eutectic with interlamellar spacing of about 5μm. The Ni_3B lamellae are twice the size of the Ni lamellae. However, this interlamellar spacing is 10 times larger than that observed on the same eutectic quenched ($T=10^0Cs^{-1}$) from the liquidus (Fig 2). In this quenching mode, the Ni and Ni_3B lamellae have the same size (0.5μm). In this latter mode of cooling, figure 3 shows the transmission electron micrograph (a), the superposed diffraction pattern (b) as well as the key diagram (c) of the eutectic.

The change in microstructure of the meltspun eutectic as a function of the wheel velocity is presented on Figure 4. Figures 4a and b show the lamellar eutectic structure at wheel velocity, $V_r = 15ms^{-1}$ and $28ms^{-1}$ respectively although with varying interlamellar spacing. The eutectic structure remains perfectly lamellar for wheel velocities less than or equal to $28ms^{-1}$. At $28 < V_r < 45ms^{-1}$, the lamellar eutectic becomes fine. However, at $V_r \geq 45ms^{-1}$ the eutectic is no more lamellar but globular as shown in Figure 4c. This structure arises from the very high cooling rate ($T > 10^6Ks^{-1}$). As reported by Cantor (1986), the higher the wheel velocity the higher is the cooling rate.

As mentioned above, in the eutectic quenched from the liquidus, the lamellae of Ni and Ni_3B have the same size (Fig. 2). However, in the case of the meltspun Ni – Ni_3B eutectic, the lamellae no longer have the same size. Thus for the wheel velocity of about $15ms^{-1}$, the interlamellar distance is about 75μm, with the lamellae of Ni_3B twice (50μm) as large as those of Nickel (25μm). Furthermore, the variation of the interlamellar spacings as a function of the cooling rate is presented in Figure 5c: From the figure, it can be deduced that the spacing decreases as the cooling rate increases. Similar observations are obtained in the plot of the interlamellar spacings as a function of the growth rate in Figure 5b.

3.2 Crystallographic Orientation of Ni(α) - Ni_3B(β)

From the superposed diffraction pattern of the two phases (under each cooling mode), the following crystallographic orientation relationship can be proposed:

(i) ***DTA mode*** (Figures 1c and d)

$$(313)_\beta \,//\, (311)_\alpha$$

$$[101]_\beta \,//\, [031]_\alpha$$

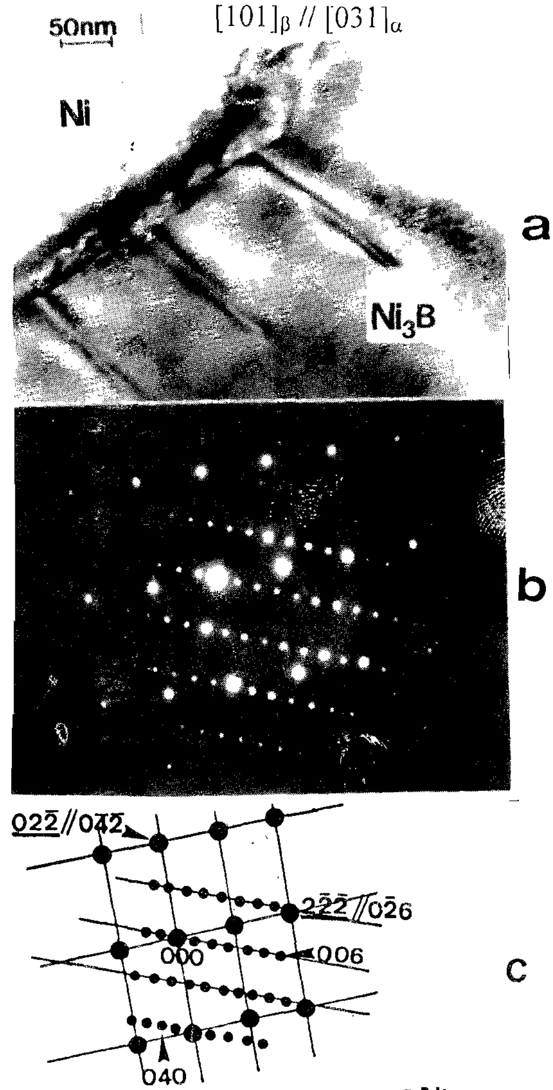

Figure 3:(a) TEM of the Ni-Ni_3B eutectic quenched from the liquidus

(b) Superposed diffraction pattern

(c) Key diagram

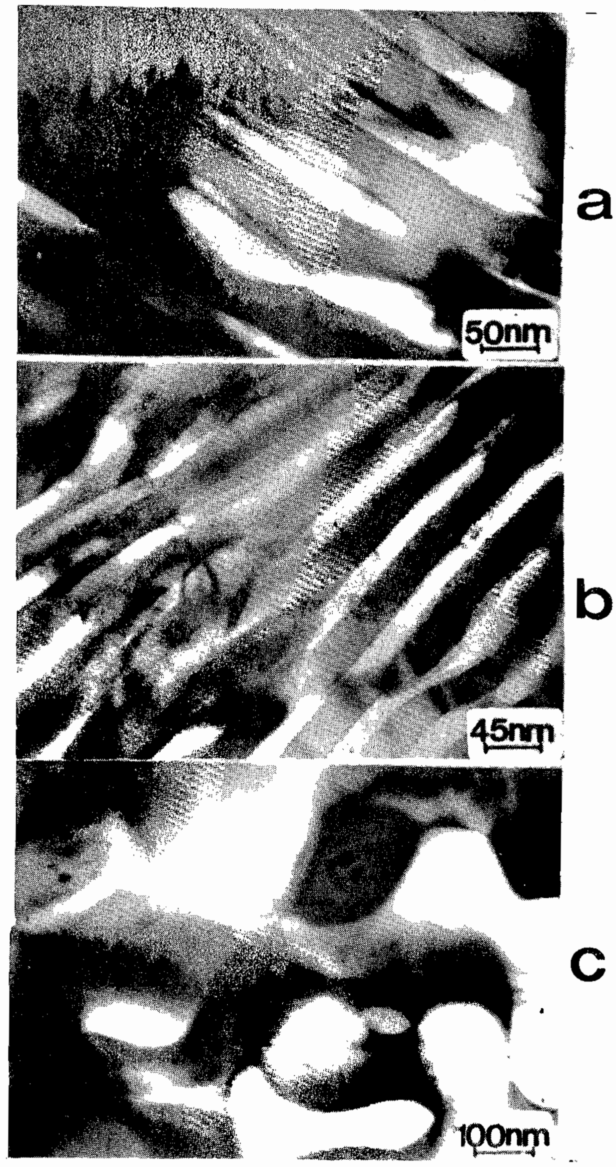

Figure 4: Evolution of the eutectic structure as function of the wheel velocity

(a) $V_r = 15ms^{-1}$ (b) $V_r = 28ms^{-1}$ (c) $V_r = 45ms^{-1}$

(ii) ***Quenching mode*** (Figures 3b and c)

$(042)_\beta \,//\, (022)_\alpha$

$(013)_\beta \,//\, (111)_\alpha$

$<100>_\beta \,//\, <211>_\alpha$

(iii) ***Meltspun mode***

$(042)_\beta \,//\, (110)_\alpha$

$<100>_\beta \,//\, <111>_\alpha$

In the slowly cooled eutectic (DTA), the orientation relationship between the two

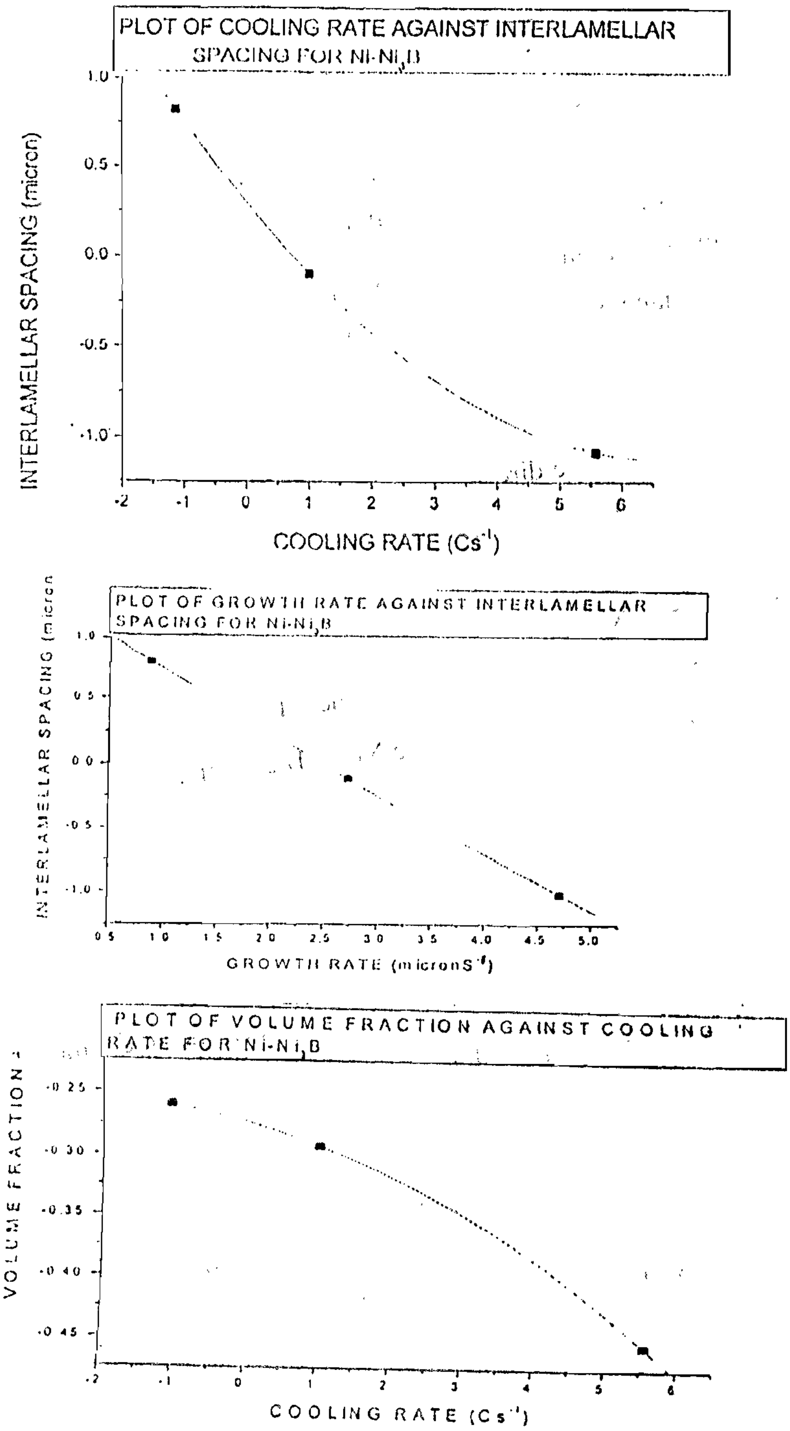

Figure 5: (a) Variation of the interlamellar distance (λ) with the cooling rates

(b) Interlamellar distance (λ) as a function of the growth rate (V) for various binary lamellar eutectics.

(c) Variation of the nickel volume fraction . (f_α), with cooling rate (T) phases is well represented by the relation given by Shapiro and Ford (Shapiro et al 1966) in unidirectionally solidified Ni – Ni_3B eutectic. The (110) Ni_3B plane is almost parallel to the (031) Ni plane. However, the two orientation relationships, in this work (quenching mode) and those of Shapiro et al 1966, are obtained from each other by a rotation of 30^0 of the (111) Ni plane around the (100) Ni_3B plane. The (111) Ni plane is parallel to the (013) and the (011) Ni_3B planes, respectively, in this work and in the report of Shapiro et al 1966. In addition, the orientation relationship between the two phases in the meltspun mode is identical to that observed in the quenching mode. The direction of the lamellae related to the surface of the ribbon is near the plane (100) of Ni_3B.

4. DISCUSSION

This discussion will be concentrated on the effect of cooling rate on the interlamellar spacing (λ) and the growth rate of the Ni-Ni_3B eutectic.

It has been reported that this eutectic remained lamellar over a range of cooling rates – from DTA to Meltspinning. Eutectic structures have been widely studied by Jackson et al (1966) and Ruth et al (1969). Theoretical approach concerning eutectic growth under slow cooling condition had been developed by Jackson et al 1966. This approach led to the expression between the interlamellar spacing (λ), undercooling (T) and the growth rate (V):

$$\Delta T = a_0/\lambda + b_0 V/\lambda \text{ -------------- (i)}$$

where a_0 and b_0 are constants characterizing the eutectic alloy.

From the above equation, if a minimum of undercooling at a maximum speed, V, is assumed, three interdependent equations between λ , V and ΔT can be obtained as follows:

$$\lambda^2 V = a_0/b_0 \text{..................(ii)}$$

$$\Delta T\lambda = 2a_0 \text{.......................(iii)}$$

$$\Delta T / V = 4a_0 b_0 \text{..............(iv)}$$

From the above relationships, the following values were estimated for the Ni – Ni_3B slowly cooled binary eutectic structure:

$$a_0 = 1.6 K.\mu m$$

$$b_0 = 1.6 x 10^{-2} K.s. \mu m^{-2}$$

According to Ruth et al (1969) the <u>pure</u> Ni-Ni_3B approaches the law $\lambda .V^{0.3}$ =

constant while the impure $Ni-Ni_3B$ follows from relation (ii). It can be deduced that the slowly cooled $Ni-Ni_3B$ eutectic in this work approached the latter theoretical law. However, at high growth rate (meltspinning), λ seemed to be independent of the cooling rate in this $Ni-Ni_3B$ eutectic. Similar observations have been reported by Liu and Fredriksson (1987) in the rapidly cooled $Fe-Fe_3C$ eutectic. Furthermore, the average growth rates (V) obtained for the slowly cooled and quenched from the liquidus $Ni-Ni_3B$ eutectic are $5\mu ms^{-1}$ and $400\mu ms^{-1}$ respectively. These values correspond to the theoretical value of '$\lambda.V^{0.5} = 10\mu m^{3/2}\ s^{-1/2}$' The measured experimental values vary between 10 and $12\mu m^{3/2}\ s^{-1/2}$. Hence there is a remarkable agreement between the theoretical and experimental values in this work.

Furthermore, for high growth rate ($4cms^{-1} \leq V \geq 7ms^{-1}$ in the meltspun $Ni-Ni_3B$ eutectic), the measured experimental value ($\lambda \approx 0.1\mu m$) seemed to be constant and twice the theoretical value of 0.05μm. This probably shows that this theoretical law seems to be invalid for meltspun eutectic. However, Jackson and Hunt (1966) model has been modified by Kurz et al (1986) and Trivedi et al (1987) in order to adapt it for high growth rates such as observed in meltspinning.

Moreover, it was observed that the volume fraction (f_α) of Ni decreased as the cooling rate increased (Figure 5c). This is in good agreement with the observations of Liu and Fredriksson 1987 in the Fe – C alloys.

5. CONCLUSION

It has been shown in this work that the theoretical law "$\lambda^2 V$ = constant" between the interlamellar distance (λ) and the growth rate (V) is valid for slow cooling rates. For high cooling and growth rates (meltspinning) this law tends towards the stability of λ .

We also reported a decrease of the volume fraction of Ni as the cooling rate increased, a behaviour similar to that reported by Liu and Fredriksson (1987) in the Fe – C alloys. Furthermore, a stable crystallographic relationship between Ni and Ni_3B phases during slow cooing in DTA were observed while this relationship approached metastability as the cooling rates increased.

ACKNOWLEDGEMENT

One of the authors, J. A., gratefully acknowledged the financial support of the French Government by way of a visiting research fellowship during the preparation of this work. He is also indebted to the Centre for Energy Research and

Development, Obafemi Awolowo University, Ile – Ife, Nigeria for granting him leave of absence.

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