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Cao, L, Cochrane, RF and Mullis, AM (2015) Microstructural Evolution and Phase Formation in Rapidly Solidified Ni-25.3 At. Pct Si Alloy. *Metallurgical and Materials Transactions A*, 46 (10). 4705 - 4715. ISSN 1073-5623

<https://doi.org/10.1007/s11661-015-3070-6>

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Microstructural evolution and phase formation in rapidly solidified Ni-25.3 at.% Si alloy

Leigang Cao^{1,a}, Robert F. Cochrane^{1,b} and Andrew M. Mullis^{1,c}

¹Institute for Materials Research, University of Leeds, Leeds LS2-9JT, UK.

^aPermanent address: School of mechanical and material engineering, North China University of Technology, Beijing 100144, China. E-mail address: caolg@ncut.edu.cn

^bE-mail address: r.f.cochrane@leeds.ac.uk

^cCorresponding author: Tel. +44 113 343 2568. Postal Address: Institute for Materials Research, School of Chemical and Process Engineering, University of Leeds, Leeds LS2-9JT, UK. Email address: a.m.mullis@leeds.ac.uk

Abstract

The drop-tube technique was used to solidify droplets of the Ni-25.3 at.% Si alloy at high cooling rates. XRD, SEM and TEM analysis revealed that the metastable phase, Ni₂₅Si₉, formed as the dominant phase in all ranges of the droplets, with γ -Ni₃₁Si₁₂ and β_1 -Ni₃Si also being present. Three different microstructures were observed: the regular and anomalous eutectic structures and near single phase structure containing small inclusions of a second phase, termed here a heteroclite structure. Both eutectic structures comprise alternating lamellae of Ni₂₅Si₉ and β_1 -Ni₃Si, which, we conjecture, is a consequence of an unobserved eutectic reaction between the Ni₂₅Si₉ and β_1 -Ni₃Si phases. The matrix of the heteroclite structure is also identified as the metastable phase Ni₂₅Si₉, in which twined growth is observed in the TEM. As the cooling rate is increased (particle size decreased) the proportion of droplets displaying the entire heteroclite structure tends to increase, with its fraction increasing from 13.91% (300-500 μ m) to 40.10% (75-106 μ m). The thermodynamic properties of the Ni₂₅Si₉ phase were also studied by in-situ heating during XRD analysis and by DTA. This showed the decomposition of Ni₂₅Si₉ to β_1 and γ -Ni₃₁Si₁₂ for temperatures in excess of 790 K (517 °C).

Keywords: Intermetallics; Phase Transformation; Rapid-solidification; Microstructure.

1. Introduction

Intermetallic compounds have been paid great attention for their potential application as high temperature structural materials, due to the possibility of combining the ductility of metals and the strength and oxidation resistance of ceramics [1]. One such is the $\beta\text{Ni}_3\text{Si}$ compound, noted for its high melting point, excellent oxidation resistance and high strength at elevated temperatures. However, like many other intermetallics, its limited room temperature ductility restricts its application owing to the difficulty in fabricating engineering components via conventional processing routes [2-6]. A number of trials have been carried out to improve its ductility and a significant body of fundamental research into phase formation and microstructural evolution under different processing conditions has been amassed. One potential route to overcome this difficulty is to form intermetallic-metal matrix composites by incorporating a ductile phase into the brittle matrix, or by solidifying a ductile phase directly from the parent melt, to form a so-called *in-situ* composite [1, 7].

At the Ni-rich end of the Ni-Si phase diagram, which is shown in Fig.1, the main phases present are $\alpha\text{-Ni}$ and the intermetallics $\beta\text{-Ni}_3\text{Si}$, $\gamma\text{-Ni}_{31}\text{Si}_{12}$ and $\delta\text{-Ni}_2\text{Si}$. β occurs in three forms, a low temperature polymorph, β_1 , which has the $L1_2$ crystal structure and two high temperature forms, β_2 and β_3 , both of which have the $D0_{22}$ crystal structure, with β_2 being an ordered form of β_3 . Çadırlı et al. [9] produced four arc-melted samples with Si composition being 10, 21.4, 25 and 35 at.%. Subsequent mechanical testing indicated that the micro-hardness increased with increasing Si content. Layered composite structures consisting of $\alpha\text{-Ni}$ and $\beta_1\text{-Ni}_3\text{Si}$ have also been obtained using directional solidification techniques [10-13]. Milenkovic et al. [13] concluded that the micro-hardness decreased in the sequence Ni_3Si , $\text{Ni-Ni}_3\text{Si}$ eutectic (as-solidified) and $\text{Ni-Ni}_3\text{Si}$ eutectic (directionally solidified), indicating the latter, layered composite, might possess higher ductility.

Another potential route to improve this lack of formability is non-equilibrium processing via rapid solidification, with the resulting refined grain structure [14-16] and the presence of anti-phase domains and disorder-order structures improving ductility [17, 18]. Moreover, in this route annealing subsequent to forming can restore the desirable mechanical properties of the intermetallic. Rapid solidification can be achieved not only by rapid quenching using an external substrate, but also by rapid growth into the bulk undercooled liquid and containerless rapid solidification, for instance via drop-tube processing. A number of non-equilibrium studies on the Ni-21.4 at.% Si alloy have been performed in order to understand the

fundamental solidification mechanism. The highest undercooling of this material, at 550 K (550 °C), has been achieved using a glass fluxing and cyclic superheated method, wherein Liu et al. [19] and Lu et al. [20] observed a complex microstructural evolution from regular lamellar eutectic, via irregular lamellar eutectic, coarse directional dendritic to quasi-spherical eutectic colonies, and fine directional dendrite to superfine anomalous eutectic. Significant grain refinement was observed with increased undercooling [21], which they attributed to enhanced nucleation, although many other mechanisms have also been suggested to account for this phenomenon in deeply undercooled melts, including post-recalcence remelting [22] and the development of growth instabilities [23, 24]. Conversely, a study by Goetzing et al. [25] attained a regular eutectic microstructure for $\Delta T < 30$ K (30 °C), which was then progressively replaced by an anomalous eutectic microstructure as the undercooling is increased, with the transition being complete at $\Delta T > 150$ K (150 °C). Similar to the samples produced by arc-melting or directional solidification, only α -Ni and β_1 -Ni₃Si were present in these alloys. Conversely, when high cooling rates were applied, for instance in the studies by Leonhardt et al. [8] and Dutra et al. [26], the metastable phase Ni₂₅Si₉ was observed.

The direct solidification of β -Ni₃Si from a melt of the same composition has been studied by Ahmad et al. [27], who performed undercooling experiments on a Ni-25.3 at% Si alloy using a melt-fluxing technique. On the basis of the phase diagram (Fig. 1), the equilibrium solidification path from the Ni-25.3 at.% Si melt would be for the growth of γ -Ni₃₁Si₁₂, with the subsequent conversion to β_3 via a peritectic reaction below 1443 K (1170 °C). As the temperature is further decreased, β_3 will undergo an ordering reaction to form β_2 , which itself will decompose via a eutectoid reaction to give $\beta_1 + \gamma$. With the γ -liquidus at this composition estimated at 1496 K (1223 °C) direct access to β_3 should become possible for undercoolings of ≈ 53 K (53 °C) or above. However, despite obtaining the required undercooling Ahmad et al. were unable to obtain single-phase β -Ni₃Si. Instead, at all undercoolings, the solidification was always to a lamellar eutectic structure of single-phase γ -Ni₃₁Si₁₂ and a Ni-rich lamella consisting of a fine, eutectoid dispersion of α -Ni and β_1 . The measured growth velocities were extremely low, with a maximum of 0.018 m s⁻¹ at a maximum undercooling of 160 K (160 °C), which is consistent with the general trend revealed by previous studies on the Ni-Si alloys that the solidification velocity drops with increasing Si concentration [8, 28]. Ahmad et al. also noted an exceptionally high apparent viscosity in the melt, which may be due to the Si acting as a network former, and a general resistance to nucleation of the melt. In addition,

small amounts of β_3 and the metastable phase $\text{Ni}_{25}\text{Si}_9$ were retained in the as-solidified structure, despite the low cooling rate, estimated at $<10 \text{ K s}^{-1}$.

Recently, studies on Ni-29.8 at.% Si eutectic alloy were carried out by Lu et al., who obtained a small amount of amorphous phase at an undercooling in excess of 240 K (240 °C) with a cooling rate of $\approx 1 \text{ K s}^{-1}$ [29], indicating a very low cooling rate for amorphous phase formation in a binary alloy. The formation of the amorphous phase here might be because the Ni-29.8 at.% Si melt, like the Ni-25.3 at.% Si studied by Ahmad et al., has an anomalously high viscosity [27]. In this paper we focus on Ni-25.3 at.% Si alloy which has been rapidly solidified by processing in a 6.5 m drop tube, wherein free-fall solidification and rapid in-flight cooling can be achieved. This technique is an effective method to form and retain non-equilibrium phases, e.g. supersaturated solid solution, metastable phase and metallic glass [14], due to the high undercoolings likely through melt sub-division and the high post-recalescence cooling rates achieved. This extends our previous work on this alloy by both melt undercooling [27], wherein a eutectic structure between α and γ was observed and drop tube processing, wherein a previously unobserved $\beta_1 - \text{Ni}_{25}\text{Si}_9$ eutectic was detected [30, 31]. However, in these previous drop-tube studies microstructural characterisation was limited to relatively large droplets (mean diameter = 400 μm), wherein only one type of microstructure was identified. In comparison we here extend the work to significantly smaller particles (mean diameter for smallest size fraction = 90 μm), which gives access to cooling rates that are at least one order of magnitude higher. Consequently, two further microstructures have been identified, one of which is essentially single phase $\text{Ni}_{25}\text{Si}_9$. This has also permitted, for the first time, a study into the thermal decomposition of $\text{Ni}_{25}\text{Si}_9$, using DTA and XRD analysis with *in situ* heating. Moreover, a much larger number of droplets has now been collected and analysed, permitting a statistical analysis of microstructure as a function of cooling rate, wherein we are able to determine that the previously observed $\beta_1 - \text{Ni}_{25}\text{Si}_9$ eutectic is associated with low undercooling in the free-falling droplets while the new structures are associated with high undercooling.

2. Experimental

Ni-25.3 at.% Si alloy was prepared by arc-melting its elemental constituents (purity = 99.99% Ni, 99.999% Si) under a protective argon atmosphere, this process being repeated 5 times to ensure uniform mixing of the final sample. The ingot was weighed after each arc-melting cycle to check for mass loss and the final composition of the ingots was checked by EDX to

ensure that the composition of the material used for drop-tube processing had not deviated from its notional value.

The alloy was loaded into an alumina crucible with 3 laser drilled holes (300 μm diameter) in the base. The crucible was placed in a RF coil fixed at the top of the 6.5 m drop tube, which was filled to a pressure of 50 kPa with dried, oxygen free N_2 gas, having previously been flushed multiple times with N_2 and evacuated to a pressure of 4×10^{-3} Pa. The alloy was heated by induction of heating of a graphite susceptor. Temperature determination was by means of an R-type thermocouple inside the melt crucible. When the desired superheat was achieved the melt was sprayed by pressurising the crucible with 4×10^5 Pa of N_2 gas. The spherical droplets with diameters in the range of 75-850 μm were collected at the bottom of the drop tube and classified into several size groups. The size of the sieves used here are 850 μm , 500 μm , 300 μm , 212 μm , 150 μm , 106 μm , 75 μm . In total 3 separate batches of powder were produced in order to conduct the analysis reported below. For particle sizes of 150 μm and above the material from each batch of powder was analysed separately. No significant differences were found to exist between the separate batches and typical results are presented. For particle sizes of 106 μm and below, once the average composition of the particles had been checked the powders from the 3 batches were combined for subsequent analysis due to the small mass of fine powder produced in each run.

The particles of each group size were hot mounted using Transoptic resin. The mounted samples were ground flat using a series of progressively finer SiC papers starting with 240, 400, 800 and lastly 1200 grit, with optical microscopy being used to check the quality of the surface finish at each stage. Once the samples were appropriately ground they were polished using 6 μm , 3 μm , 1 μm and 0.25 μm diamond paste. The samples were washed using dilute detergent and methanol and then dried using hot air between each polishing step.

The composition of the polished samples was characterized using EDX detection mounted on a LEO 1530 Gemini FEGSEM. Once EDX analysis was complete the polished samples were etched using here a mixture of Hydrofluoric Acid (5ml), Hydrogen Peroxide (5ml) and water (10ml) to reveal the microstructure for further SEM analysis. FIB was used to prepare the TEM specimens, which were analysed subsequently using an FEI Tecnai F20 FEG-TEM.

XRD analysis, including XRD with *in-situ* heating, was conducted to identify the phase constitution of the samples and any thermally mediated transformations of the metastable phases (Cu K_α radiation, P'ANalytical X'Pert MPD, Almelo, The Netherlands). *In-situ*

heating was performed in a sealed chamber at high vacuum ($\approx 1.68 \times 10^{-4}$ Pa), in which the sample could be heated to a maximum 1473 K (1200 °C). The sample was heated from 298 K (25 °C) to around 723 K (450 °C), although it was not possible to calibrate the temperatures at which the observed phase transitions occurred. This data was therefore coupled with DTA measurements using a Perkin Elmer DTA 7, which was used to determine the onset temperature of the metastable phase transformation.

3. Results

3.1. EDX, XRD and DTA analyses

At least 10 particles in each size range, with at least 3 from each of the three batches of powder, were checked by EDX in order to determine the average composition of the droplets. These measurements were within the range 24.97-25.46 at.% Si, indicating that in all size ranges the particles have average compositions close to the nominal composition.

Fig. 2 shows the XRD patterns of the Ni-25.3 at.% Si droplets as a function of particle size. It can be seen that all of the resulting diffraction patterns, even for the smallest particles (highest cooling rate), show the same general trend, namely the presence of three main phases: Ni₂₅Si₉ (metastable phase), γ -Ni₃₁Si₁₂ and β_1 -Ni₃Si.

Here, a couple of comments relating to the phases present may be pertinent. Ni₇₄Si₂₆ is a known stacking variant of Ni₂₅Si₉ [32]. Although the lattice constants 'a' and 'b' are same, the 'c' value of Ni₇₄Si₂₆ (c=28.855 Å) is three times of that of Ni₂₅Si₉ (c=9.618 Å). It is therefore difficult to identify Ni₇₄Si₂₆ in co-existence with Ni₂₅Si₉. Moreover, the structure and diffraction data of Ni₇₄Si₂₆ are incomplete. Therefore, in the present work, the metastable phase is referred to as Ni₂₅Si₉ for the purposes of analysis and discussion, but has previously been interchangeably referred to as either Ni₇₄Si₂₆ or Ni₂₅Si₉ by other authors. Moreover, it is also difficult to distinguish the α -Ni and β_1 -Ni₃Si phases, because both phases have the same cubic structure, with the lattice constant 'a' being 3.5244 Å and 3.5050 Å, respectively. A number of previous studies on Ni-Si alloys [8, 33] have shown overlapping α -Ni and β_1 -Ni₃Si XRD peaks. Here, the β_1 -Ni₃Si phases can only be confirmed according to the presence of the unique, but weak, characteristic peaks corresponding to the (100) and (110) planes at 3.5050 Å and 2.4784 Å. These peaks were only identified in the 500-850 μ m size fraction (Fig. 2). In addition, neither β_2 nor β_3 were identified in any size range.

In order to obtain an accurate temperature determination for the phase transformation of $\text{Ni}_{25}\text{Si}_9$, DTA analysis was performed on the 300-500 droplets with heating rate of 20 K min^{-1} , the results of which are shown in Fig. 3. The curve for the first cycle displays an exothermic reaction near 789 K (516 °C), which is ascribed to the transformation of the metastable $\text{Ni}_{25}\text{Si}_9$ phase. On the basis of the equilibrium phase diagram, the endothermic peaks near 1281 K (1008 °C) and 1337 K (1064 °C) may be related to the $\beta_1 + \gamma \rightarrow \beta_2$ and the $\beta_1 \rightarrow \alpha\text{-Ni} + \beta_2$ transformation, respectively. The strong peak at 1406 K (1133 °C) is due to the $\beta_2 \rightarrow \beta_3$ transformation. The peaks at 1496 K (1223 °C) and 1519 K (1246 °C) represent the peritectic reaction and final melting respectively. The temperature departures of these reactions from the equilibrium phase diagram are listed in Table 1. There was no exothermic peak near 789 K (516 °C) during the second heating cycle, implying that the metastable phase transformed completely. Fig. 4 shows the results of the *in-situ* XRD heating experiment on the 300-500 μm droplets, indicating a gradual phase transformation at elevated temperatures. Comparing the XRD patterns of the sample before and after heat treatment at 298 K (25 °C), it indicates that the metastable $\text{Ni}_{25}\text{Si}_9$ phase converted fully to $\beta_1\text{-Ni}_3\text{Si}$ and $\gamma\text{-Ni}_{31}\text{Si}_{12}$.

3.2.SEM and TEM analysis

Microstructural analysis reveals that the majority of droplets can be classified as containing one or more of three typical structures. As shown in Fig. 5 these comprise two eutectic structures – regular (I) and anomalous (II) and one two-phase but non-eutectic structure which we here term the heteroclite structure (III). Moreover, three single phase morphologies were also observed: M_1 - an extended single phase (Fig. 6); M_2 – a phase that grows continuously throughout the whole droplet (Fig. 7a) and M_3 – a phase that is surrounded by the regular lamellar structure (Fig. 7b). In order to determine the origin of these three typical structures (I, II and III) and three single phase morphologies (M_1 , M_2 and M_3), fine lamellar TEM specimens ($12 \times 8 \mu\text{m}$) have been prepared using the Focused Ion Beam (FIB) technique. Both the $\text{Ni}_{25}\text{Si}_9$ and $\text{Ni}_{31}\text{Si}_{12}$ phases have a complicated hexagonal crystal structure and consequently these have been identified in the TEM using the diffraction patterns corresponding to the distinguishable interplanar spacing, as shown in Table 2.

It is clear that the regular lamellar structure (I) comprises two phases. A clear lamellar nanostructure may be observed in the TEM bright field micrograph shown in Fig. 8. This shows alternating regular lamellae comprising wide ($\approx 200 \text{ nm}$) and narrow ($\approx 20 \text{ nm}$) bands. Due to the similar structures of $\alpha\text{-Ni}$ and $\beta_1\text{-Ni}_3\text{Si}$, direct phase confirmation of the narrow

bands has not been achieved. However, from Fig. 8 it is clear that the thin bands are continuous with, and therefore the same phase as, the single phase regions embedded within the lamellar structure. A selected area diffraction pattern confirms that this single phase region, and therefore the thin lamellae, are the intermetallic phase $\beta_1\text{-Ni}_3\text{Si}$. A similar selected area diffraction pattern confirms that the wide lamellar phase is metastable phase $\text{Ni}_{25}\text{Si}_9$.

The anomalous eutectic structure (II) and the single phase (M_1) were also analyzed by TEM, as shown in Fig. 9. The TEM selected area diffraction patterns confirm that the irregular eutectic structure (II) also comprises the metastable $\text{Ni}_{25}\text{Si}_9$ and stable $\beta_1\text{-Ni}_3\text{Si}$ phases. Therefore, the structures, I and II, are composed of the same phases. The single phase M_1 was identified as the $\gamma\text{-Ni}_{31}\text{Si}_{12}$ phase.

The heteroclite structure (III) also comprises two phases, with a small volume of a fine phase with a curved morphology dispersed in a dominant matrix phase. The selected area diffraction pattern confirms that the coarse matrix is the metastable $\text{Ni}_{25}\text{Si}_9$ phase (Fig. 10). Twinned growth was also confirmed from the TEM analysis. The thickness of the fine phase is typically less than 20 nm and it is therefore difficult to confirm its identity. The phases M_2 and M_3 are identified as $\beta_1\text{-Ni}_3\text{Si}$ and $\text{Ni}_{25}\text{Si}_9$ respectively (Fig. 11 a and b). Moreover, the phase next to $\beta_1\text{-Ni}_3\text{Si}$ is also identified as $\text{Ni}_{25}\text{Si}_9$, which also supports the co-growth mechanism of $\text{Ni}_{25}\text{Si}_9$ and $\beta_1\text{-Ni}_3\text{Si}$ under non-equilibrium conditions.

One particle in which the heteroclite structure (III) was the only morphology present was selected for heat treatment, wherein it was held for 30 minutes at 867 K (594°C) under a protective nitrogen atmosphere. The microstructure after heat-treatment (Fig. 12a) shows the fine phase I_1 dispersed in a matrix (I_2). These two phases were identified as $\gamma\text{-Ni}_{31}\text{Si}_{12}$ (I_1) and $\beta_1\text{-Ni}_3\text{Si}$ (I_2) by TEM, as shown in Fig. 12b. This is consistent with the results of *in-situ* heating during XRD analysis.

In order to study the microstructural evolution with decreasing particle size, the droplets are classified into two different categories (A and B). Type A droplets present the entire heteroclite structure. This type of droplet were quite easily distinguishable, even with optical microscopy, once the droplets had been etched. All other droplets were classified as type B. These present a range of complicated microstructures, including various combinations of structures I, II, III, M_1 , M_2 and M_3 . An example of one such particle is given in Fig. 6 which shows a mixed structure comprising the morphologies designated I, II, III and M_1 . The fractions of type A droplet in all size fractions of the droplets have been counted. The

numbers of particles being counted are 230 (300-500 μm), 295 (212-300 μm), 304 (150-212 μm), 428 (106-150 μm) and 394 (75-106 μm). For particles of 150 μm diameter and above, particles from each of the three batches of powder were mounted separately and the count data combined as there were no significant differences between the batches. For particles below 150 μm diameter the powders were combined prior to counting. The counted results are illustrated in Fig. 13, showing that the fraction of type A droplet increases as the particle size decreases, from 13.91% (300-500 μm) to 40.1% (75-106 μm). There are no type A droplets in the 500-850 μm particles.

Within type B droplets, the anomalous structure II can be observed in all ranges of the droplets. Conversely, the fraction of the regular lamellar structure shows a decreasing trend with decreasing particle size, this structure being easily observed in large particles (212-850 μm) but almost disappearing in the 75-106 μm size fraction.

4. Discussion

From the results of microstructural evaluation described above we may conclude that the dominant phase present in all size fractions, and therefore at all cooling rates studied, is the metastable phase $\text{Ni}_{25}\text{Si}_9$.

According to previous studies [8, 27, 28] on the Ni-rich end of the Ni-Si phase diagram, it has been established that the growth velocity of the Ni-Si melts drops with increasing Si composition. The highest velocities, at 50-60 m s^{-1} ($\Delta T=250 \text{ K}$ (250 $^{\circ}\text{C}$)), were measured by Cochrane et al. [28] on pure Ni and Ni-Si melts for Si < 4.09 at.%, while the maximum for Ni-21.4 at.% Si alloy measured by Leonhardt et al. was only 1.5 m s^{-1} ($\Delta T=220 \text{ K}$ (220 $^{\circ}\text{C}$)). The extremely low growth velocity of the Ni-25.3 at.% Si melt recorded by Ahmad et al. [27] was about 0.018 m s^{-1} ($\Delta T=160 \text{ K}$ (160 $^{\circ}\text{C}$)), which is consistent with their observation of an unusually high viscosity in the melt, which they speculated might be due to the existence of structure in the liquid resulting from Si acting as a network former. Such a covalent network within the liquid would give rise to low atomic mobility and hence low growth velocity.

Under rapid solidification conditions a low atomic mobility might in turn favour the formation of phases with compositions close to that of the liquid. In this respect we note that $\text{Ni}_{25}\text{Si}_9$ has a Si concentration of 26.47 at.%, which is indeed close to that of the parent melt. A second consequence of low atomic mobility would be the restriction of long range

diffusion and the subsequent favouring of features with very fine length scales, which is indeed observed here.

Although $\text{Ni}_{25}\text{Si}_9$ was found to be the dominant phase formed in this study, the formation of $\text{Ni}_{25}\text{Si}_9$ was not observed during undercooling experiments on Ni-21.4 at.% alloys [21, 25], with only a small fraction being observed in Ni-25.3 at.% Si alloy [27]. Conversely, when high cooling rates have been applied, it was obtained in the rapidly solidified eutectic Ni-21.4 at.% Si alloys produced by Leonhardt et al. [8] by quenching the undercooled sample onto a chilled substrate and by Dutra et al. [26] using the melt-spinning technique. This seems to indicate that high cooling rates are necessary for the formation of the metastable $\text{Ni}_{25}\text{Si}_9$ phase to be observed in the as-solidified sample. Thermal analysis by DTA has indicated that the decomposition temperature for $\text{Ni}_{25}\text{Si}_9$ is 789 K (516°C), which is consistent with the observations of Leonhardt et al. [8] and Dutra et al. [26] who both identified this transition as occurring around 773 K (500 °C). Such a low decomposition temperature relative to a melting temperature of 1530 K (1230 °C) points to poor thermal stability.

One scenario that we should therefore consider is that, even if the solidification condition favours the formation of the $\text{Ni}_{25}\text{Si}_9$ phase, it would convert into the $\beta_1\text{-Ni}_3\text{Si}$ and $\gamma\text{-Ni}_{31}\text{Si}_{12}$ phases in the post-recalcescence and subsequent cooling period. This would be consistent with the retention of $\text{Ni}_{25}\text{Si}_9$ during drop-tube processing, wherein the estimated cooling rate for the coarsest size fraction, 500-850 μm , is around 500 K s^{-1} based on the model of Kasperovich et al. [34], which will largely inhibit any post-recalcescence transformations. However, XRD analysis with *in-situ* heating indicates that the metastable $\text{Ni}_{25}\text{Si}_9$ phase decomposes to $\beta_1\text{-Ni}_3\text{Si}$ and $\gamma\text{-Ni}_{31}\text{Si}_{12}$. Consequently, while it may be possible that $\text{Ni}_{25}\text{Si}_9$ formed, and subsequently underwent thermal decomposition in the undercooling experiments on Ni-21.4 at.% Si eutectic alloy [21, 25], it is not consistent with the results Ahmad et al., in which the mixed structure of $\gamma\text{-Ni}_{31}\text{Si}_{12}$ and $\beta_1\text{-Ni}_3\text{Si}$ was not observed in the resulting as-solidified samples. Instead, the $\gamma\text{-Ni}_{31}\text{Si}_{12}$ phase was formed from the undercooled liquid as the primary solidification phase and retained in the final samples. Moreover, a small fraction of $\text{Ni}_{25}\text{Si}_9$ was successfully retained, even at the very low cooling rates reported for their apparatus.

Microstructural analysis indicates that, except for the 500-850 μm droplets (completely type B), both types of the droplets (A and B) exist in all size ranges. Here, we attribute this variation to the interplay of cooling rate and undercooling. To a good first approximation,

droplets of the same size will be subjected to the same cooling rate. However, it is not true that all droplets of the same size will solidify at the same undercooling, as this is controlled by nucleation which is a stochastic process. Solidification of the liquid might be catalysed by a potent nucleation site, such as an oxide, and in such cases, deep undercooling would not be expected. However, the catalytic effect of active nuclei can be restricted by dispersing the liquid into a large number of small droplets that solidify individually [35], as is the case in the drop tube. In this stochastic process, a range of undercoolings from low to quite high would be expected in each size range of droplets due to the variation in nuclei density and potency. For a given nucleation density, the probability of a given particle containing an active nucleus decreases with decreasing volume. Consequently, high undercooling is much more likely in a population of small droplets. With reference to Fig. 13, we see that the proportion of type A droplets (entire heteroclite structure) increases with decreasing particle size, from 13.91% (300-500 μm) to 40.1% (75-106 μm). This suggests that type A droplets are the high undercooling forms. By inference, type B droplets, displaying a mixed structure, must be subject to lower undercooling.

The structures displayed by the type B droplets appear to be largely eutectic (or possibly eutectoid) in nature, which is not easily reconciled with the metastable Ni-Si diagram produced by Leonhardt et al. [8]. The bulk composition, measured by EDX analysis, is within the range 24.97-25.46 at.%, which is on the hypereutectic side of the postulated α -Ni₂₅Si₉ eutectic and between the theoretical composition of the β_1 -Ni₃Si (22.6-24.5 at.%) and Ni₂₅Si₉ (26.47 at.%) phases. Consequently, if the formation of the high temperature β_2/β_3 phases were suppressed and formation of Ni₂₅Si₉ were permitted, the expected structure would be single phase Ni₂₅Si₉ + α -Ni₂₅Si₉ eutectic where, as per the results from Ahmad et al. [27], the α -Ni maybe highly supersaturated for a deep non-equilibrium process. However, the observation here of a Ni₂₅Si₉ / β_1 -Ni₃Si eutectic, displaying both regular lamellar and anomalous eutectic structures, would imply that the metastable liquidus line for Ni₂₅Si₉ would be dropping much more steeply than is shown in Fig.1.

As mentioned above the alternative hypothesis is that the observed structure forms via a eutectoid reaction, which is attractive as the very fine structure observed appears more consistent with a solid-state, rather than liquid-solid, transformation. As can be seen from the phase diagram, there are two high temperature forms of the β -phase (disordered β_3 and ordered β_2). High cooling rates in the drop tube would be expected to favour the formation of β_3 or β_2 phases, with their subsequent decomposition giving a possible formation route for the

observed β_1 -Ni₂₅Si₉ lamellar structure. However, further analysis refutes this formation route. Firstly, XRD analysis failed to indicate the presence of any β_3 and β_2 . Some residual β_3/β_2 would be expected to remain at the highest cooling rates, particularly as Ahmad et al. [27] observed extensive retained β_3 in fluxed samples in which a cooling rate $< 10 \text{ K s}^{-1}$ was attained. Secondly, the microstructural analysis also failed to observe the potential mixed structure of the β_1 -Ni₃Si + γ -Ni₃₁Si₁₂, which might be expected via the eutectoid reaction, $\beta_2 \rightarrow \beta_1 + \gamma$ (according to the equilibrium phase diagram) if this assumption is correct. Moreover, a eutectoid reaction to give β_1 -Ni₃Si + Ni₂₅Si₉ would seem highly unlikely given the poor thermal stability of Ni₂₅Si₉ and that the eutectoid temperature would be well above the measured thermal decomposition temperature for Ni₂₅Si₉. Consequently, we postulate that the observed lamellar structure formed as a result of a hitherto unobserved eutectic reaction between β_1 and Ni₂₅Si₉, with the present experimental composition close to the eutectic composition.

Further evidence for the direct growth of the observed structures from the liquid comes from the variations between structures I and II. These have the same phase constitution, β_1 -Ni₃Si and Ni₂₅Si₉, but are morphologically distinct with (I) being a regular lamellar structure and (II) being a much more disordered eutectic structure. In fact it is clear that the structure II has the features of an anomalous eutectic, a structure that is widely observed [36, 37] in the solidification of eutectic alloys from their undercooled parent melt, wherein the distinct lamellar morphology of a regular eutectic cannot be observed. Many studies [36, 37] have indicated that the fraction of anomalous eutectic structure increases with increasing undercooling. The structure II can be observed in all ranges of type B droplet, while the fraction of the regular structure (I) presents a decreasing trend with decreasing particle size and has almost disappeared in all of the 75-106 μm droplets. This is consistent with the formation of an anomalous eutectic structure resulting from solidification from an undercooled melt and hence indicates that growth occurred from the liquid via a eutectic, rather than the solid via a eutectoid, reaction.

In some eutectic systems, e.g. Ag-Cu [37] and Ni-Sn [38], the coupled eutectic growth will break down in favour of single phase growth if the liquid experiences sufficiently high undercooling. According to the metastable phase diagram (Fig. 1), at high undercooling the Ni-25.3 at.% Si droplets might solidify directly to the Ni₂₅Si₉ phase, with only a small residual of another phase. Type A structures might therefore arise in droplets that have been

undercooled below the metastable extension of the $\text{Ni}_{25}\text{Si}_9$ solidus line, wherein the droplets solidify entirely to the heteroclitite structure in which the primary solidification of $\text{Ni}_{25}\text{Si}_9$ occurs.

It can be summarized that at moderate cooling rates the Ni-25.3 at.% Si alloy solidifies to $\beta_1\text{-Ni}_3\text{Si} + \text{Ni}_{25}\text{Si}_9$ via a previously unobserved eutectic reaction while at high cooling rates and high undercooling it solidifies to almost single phase $\text{Ni}_{25}\text{Si}_9$. This behaviour is not only different from the prediction of the phase diagram, but also different from the studies by Ahmad et al. [27], who observed a eutectic structure between $\gamma\text{-Ni}_{31}\text{Si}_{12}$ and supersaturated $\alpha\text{-Ni}$ with complete suppression of β -phase solidification from the melt. This has strong parallels with work on Nb-xSi ($x = 21.0\text{-}27.0$ at.%) alloys by Bertero et al. [39], who performed a series of experiments using levitation techniques, which in some cases were combined with splat quenching of the undercooled melt. Contrary to the prediction from the phase diagram that direct solidification to primary Nb_3Si should be possible for undercoolings in excess of 270 K (270 °C), they observed solidification was to a metastable $\alpha\text{-Nb}$ and $\beta\text{-Nb}_5\text{Si}_3$ eutectic in levitated samples. Conversely, the formation of Nb_3Si was observed in splat quenched samples, which, as they described, was independent of the undercooling prior to splat quenching. They attributed this phenomenon to difficulty in nucleating the Nb_3Si phase, which can grow at high cooling rate due to enhanced short-range diffusion and possibly heterogeneous nucleation sites on the splat. Therefore, it is not without precedent that high cooling rates should be the deterministic factor in the formation of the single phase structures in materials in which the short-range diffusion is preferential. This is also consistent with the nanostructure morphology in $\beta_1\text{-Ni}_{25}\text{Si}_9$ eutectic structures with narrow lamellae spacings.

There is one further common characteristic in the solidification of Nb-25 at.% Si and Ni-25.3 at.% Si alloys at high undercooling and high cooling rate, namely the suppression of the peritectic reaction. In the initial stage of the peritectic reaction the primary phase is expected to be coated by a thin layer of the peritectic phase with the subsequent reaction being a diffusion-controlled process [40], with diffusion occurring through the growing solid layer of the peritectic phase. Alternatively, St. John et al. [41] pointed out that some degree of undercooling was necessary in the peritectic reaction, which will also favour the direct crystallization of the secondary phase from the liquid. This mechanism was supported by Barker and Hellowell [42], who concluded that in Pb-Bi alloys, the primary Pb-rich phase was inefficient as a heterogeneous nucleant for the secondary phase and that the nucleation of

the secondary phase took place at many other sites in the Pb-Bi liquid. The observation of Nb₃Si formation at high cooling rate by Bertero et al. might be a consequence of the second mechanism. In the undercooling study of Ahmad et al., a small amount of β₃ phase was observed in fluxed samples, however the primary solidification was always the eutectic growth of γ-Ni₃₁Si₁₂ and supersaturated α-Ni. In the present work, we have found no evidence for formation of either the β₃ or β₂ phases, despite the high cooling rates which would be expected to favour their retention in the as-solidified droplets. This might be because the peritectic reaction is completely suppressed and the nucleation of β₃ and β₂ from the liquid is difficult.

Rapid solidification at high cooling rates is an effective route to the formation metallic glass, especially for deep eutectic melts [14] as this reduces the normalised glass transition temperature. Recently, Lu et al. [29] obtained small amounts of an amorphous phase in bulk eutectic Ni_{70.2}Si_{29.8} alloy under slow cooling conditions (about 1 K s⁻¹). Meanwhile, in the Nb-Si system, Benderdky et al. formed an amorphous phase in the narrow region adjacent to the chill surface in melt-spinning experiments on Nb-25 at.% Si alloy [43], indicating that at high cooling rates melts other than those of eutectic composition can be frozen into the amorphous state. However, in this study no evidence for an amorphous phase was observed, even in the smallest particle range. This may be because of the presence of the crystalline phases Ni₂₅Si₉ and β₁-Ni₃Si with compositions very close to that of the parent melt. Conversely, the condition is different for the Nb-Si alloys, in which the formation of the stable phases, α-Nb (<3.44 at.% Si) and α-Nb₅Si₃ (37.5-38.6 at.% Si) requires long-range diffusion.

5. Conclusions

The following conclusions can be derived from the present investigation.

1. Three phases are obtained in the drop tube solidified Ni-25.3 at.% Si droplets, β₁-Ni₃Si, γ-Ni₃₁Si₁₂ and Ni₂₅Si₉, with Ni₂₅Si₉ being the dominant phase in all ranges of the droplets.
2. There is strong evidence for the existence of a previously unobserved β₁ – Ni₂₅Si₉ eutectic, with the eutectic composition being close to the composition of the starting alloy, namely Ni-25.3 at.% Si.
3. At high undercooling the droplets appear to be possible to bypass the newly identified eutectic and form a near single phase Ni₂₅Si₉ structure (heteroclite structure). The fraction of

the droplets with entire heteroclitite structure increases with decreasing particle size, from 13.91 % in the 300-500 μm size range to 40.1% in the 75-106 μm size range.

4. The metastable phase $\text{Ni}_{25}\text{Si}_9$ decomposes to the stable phases, β_1 and $\gamma\text{-Ni}_{31}\text{Si}_{12}$, with the onset transformation temperature being around 789 K (516°C) at the heating rate of 20 K min^{-1} .

Acknowledgements

The authors acknowledge financial supports of the China Scholarship Council (CSC) – University of Leeds scholarship program.

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Table 1. The detected and the theoretical temperatures for the reaction observed in the DTA analysis

Reaction	Detected temperature K (°C)	Theoretical temperature ^d K (°C)	ΔT K (°C)
$\beta_1 + \gamma \rightarrow \beta_2$	1281 (1008)	1263 (990)	18 (18)
$\beta_1 \rightarrow \alpha\text{-Ni} + \beta_2$	1337 (1064)	1308 (1035)	29 (29)
$\beta_2 \rightarrow \beta_3$	1406 (1133)	1388 (1115)	18 (18)
$\alpha + \beta_3 \rightarrow L$	1433 (1160)	1416 (1143)	17 (17)
$\beta_3 \rightarrow \gamma + L$	1496 (1223)	1443 (1170)	53 (53)

^dThe theoretical temperatures are referred to the equilibrium phase diagram.

Table 2. Some standard XRD diffraction data of the Ni₃₁Si₁₂ and Ni₂₅Si₉ phases

Phase	(HKL)	d(Å)
<p>Ni₂₅Si₉</p> <p>Hexagonal, P-3, 147 a=b=6.6980 Å, c=9.6180 Å $\alpha=\beta=90^\circ$, $\gamma=120^\circ$</p>	001	9.6180
	100	5.8000
	101	4.9672
	002	4.8090
<p>Ni₃₁Si₁₂</p> <p>Hexagonal, P321, 150 a=b=6.6777 Å, c=12.2800 Å $\alpha=\beta=90^\circ$, $\gamma=120^\circ$</p>	001	12.280
	002	6.1400
	100	5.7831
	101	5.2319

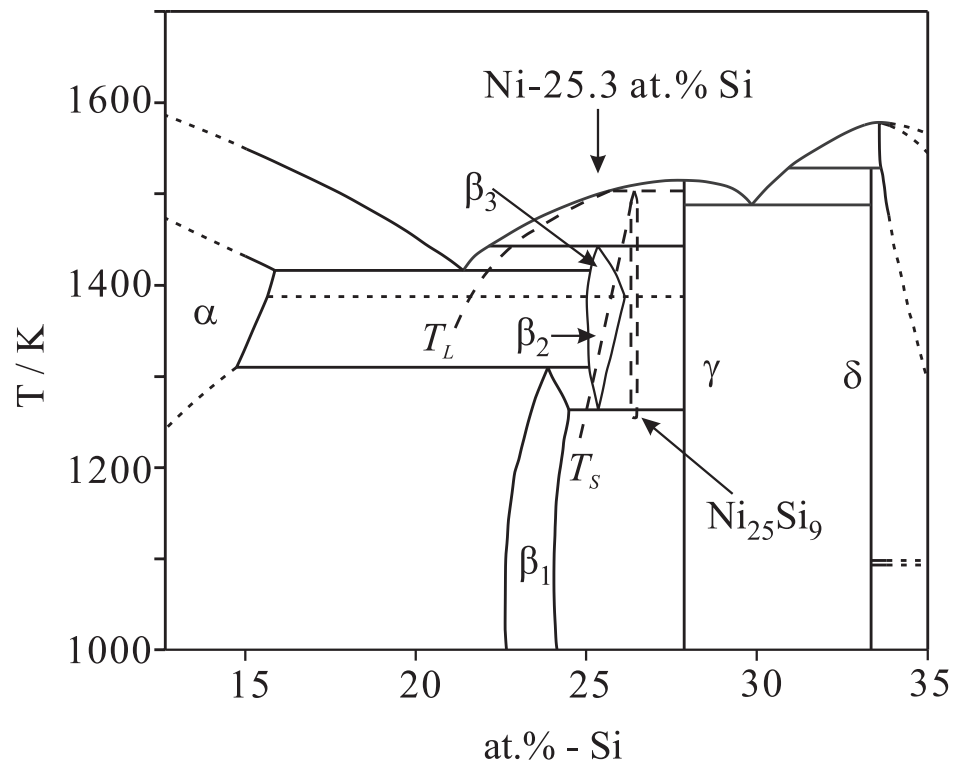


Fig. 1. Ni-rich part of Ni-Si binary phase diagram with the metastable phase Ni₂₅Si₉ [8].

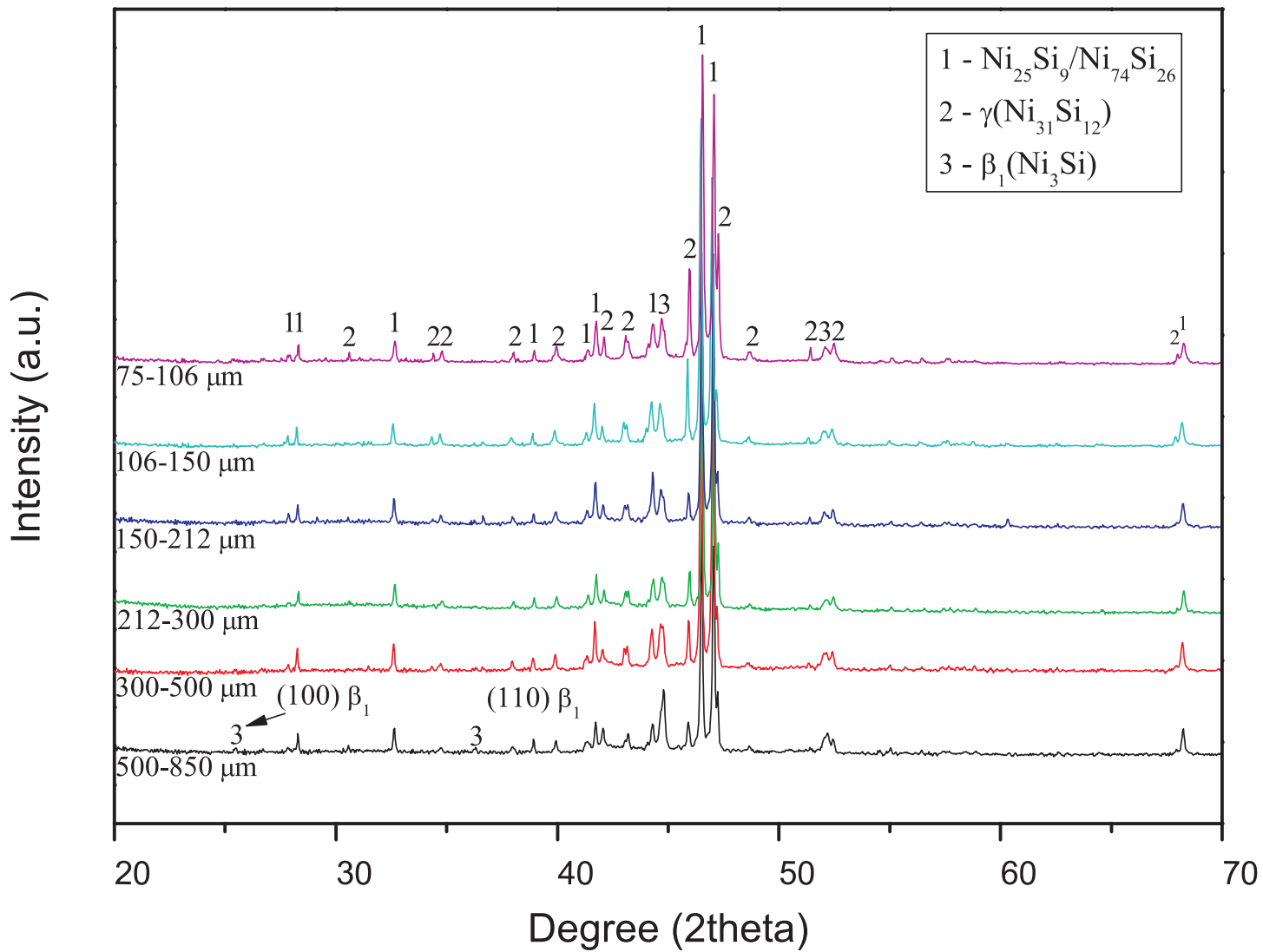


Fig. 2. XRD diffraction patterns for the Ni-25.3 at.% Si drop tube solidified samples as a function of particle size range.

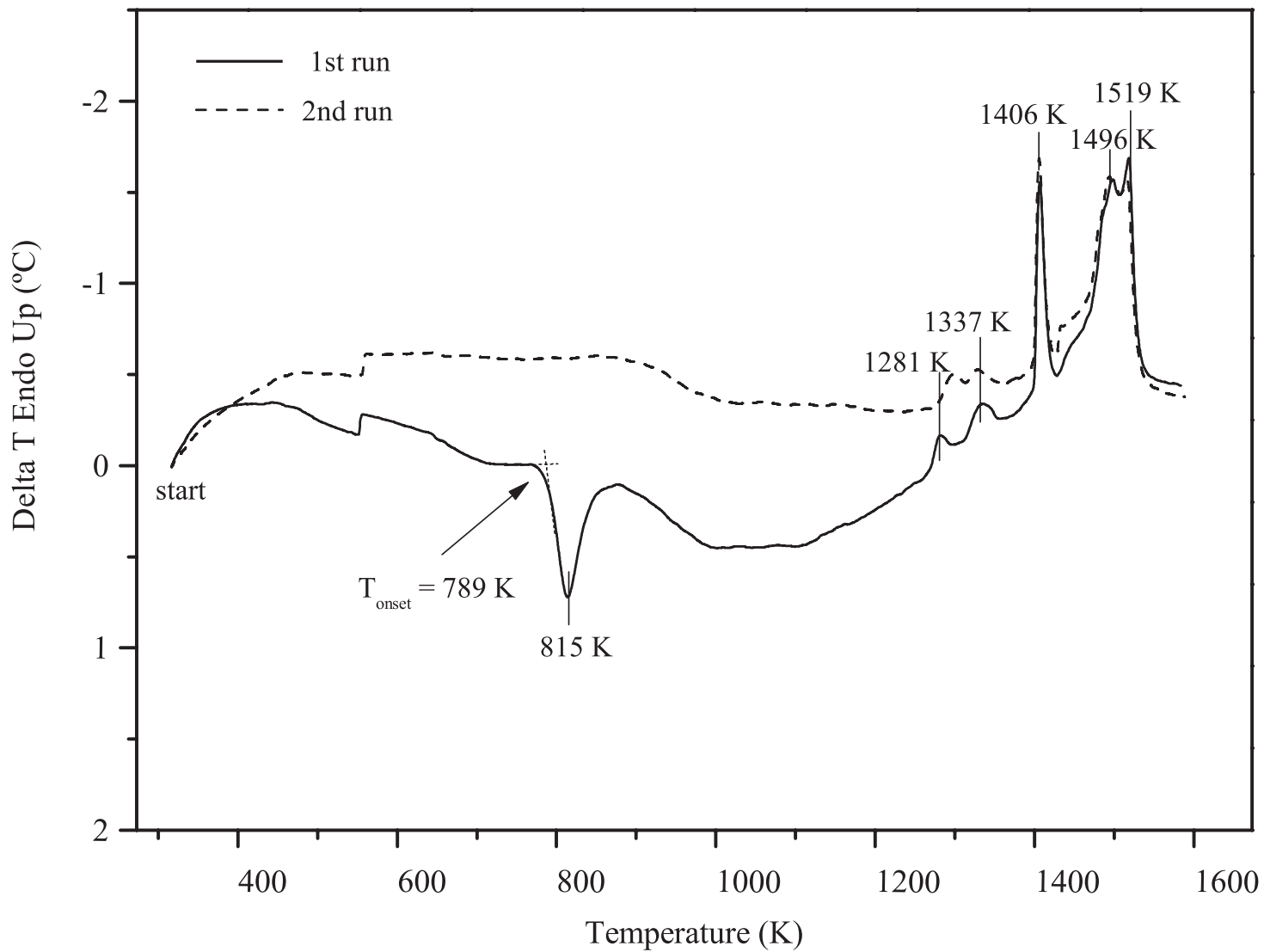


Fig. 3. DTA curves of the 300-500 μm droplets with the heating rate being 20 K min^{-1} . There is an exothermic reaction at 789 K (516 $^{\circ}\text{C}$) in the first heating process corresponding to the thermal decomposition of the $\text{Ni}_{25}\text{Si}_9$ phase.

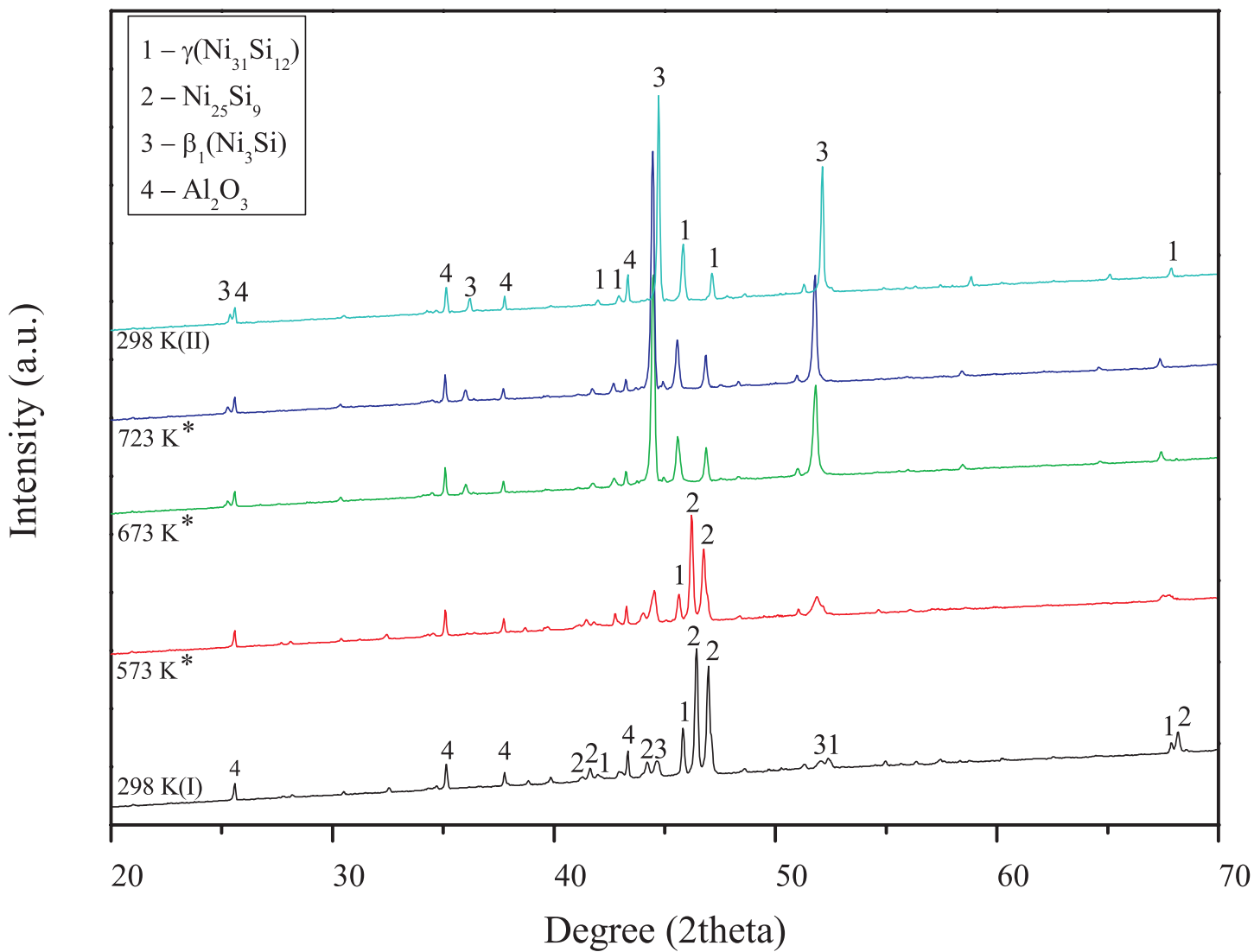


Fig. 4. Results of the *in-situ* heating of 300-500 μm Ni-25.3 at.% Si droplets during XRD analysis. Samples were heated from 298 K(I) (25 $^{\circ}\text{C}$) to above the $\text{Ni}_{25}\text{Si}_9$ decomposition temperature and then cooled down again to 298 K(II) (25 $^{\circ}\text{C}$). The peaks corresponding to $\text{Ni}_{31}\text{Si}_{12}$ (1), $\text{Ni}_{25}\text{Si}_9$ (2), $\beta_1\text{-Ni}_3\text{Si}$ (3) and Al_2O_3 (4) are labelled. Characteristic peaks of Al_2O_3 are from sample holder. *The temperatures is uncalibrated, therefore the onset temperature of phase transformation is determined by DTA.

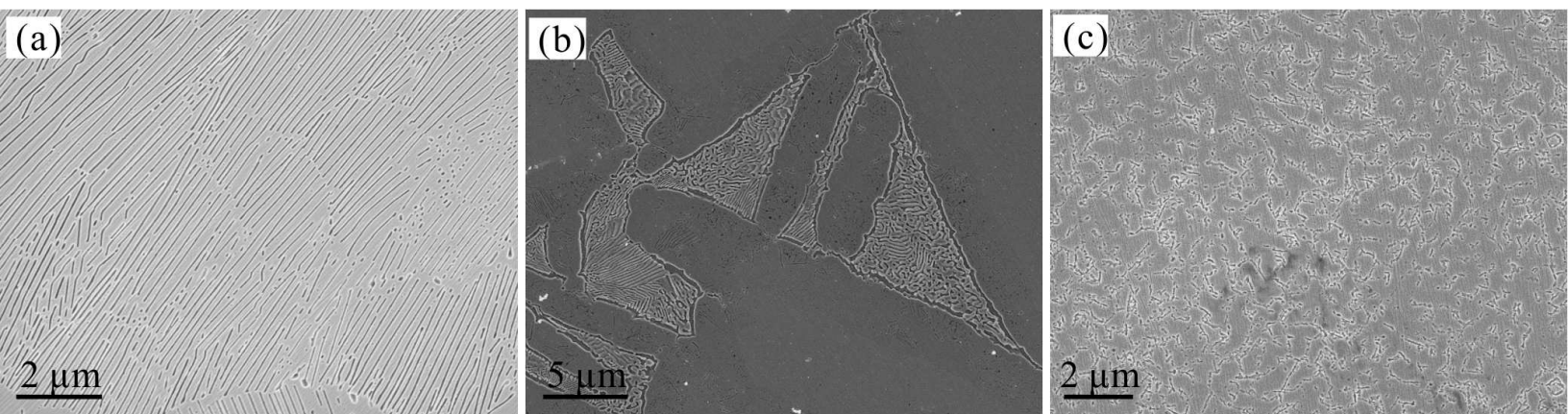


Fig. 5. SEM images of three typical structure of Ni-25.3 at.% Si drop tube samples: (a) regular eutectic structure, I; (b) anomalous eutectic structure, II; (c) heteroclitite structure, III.

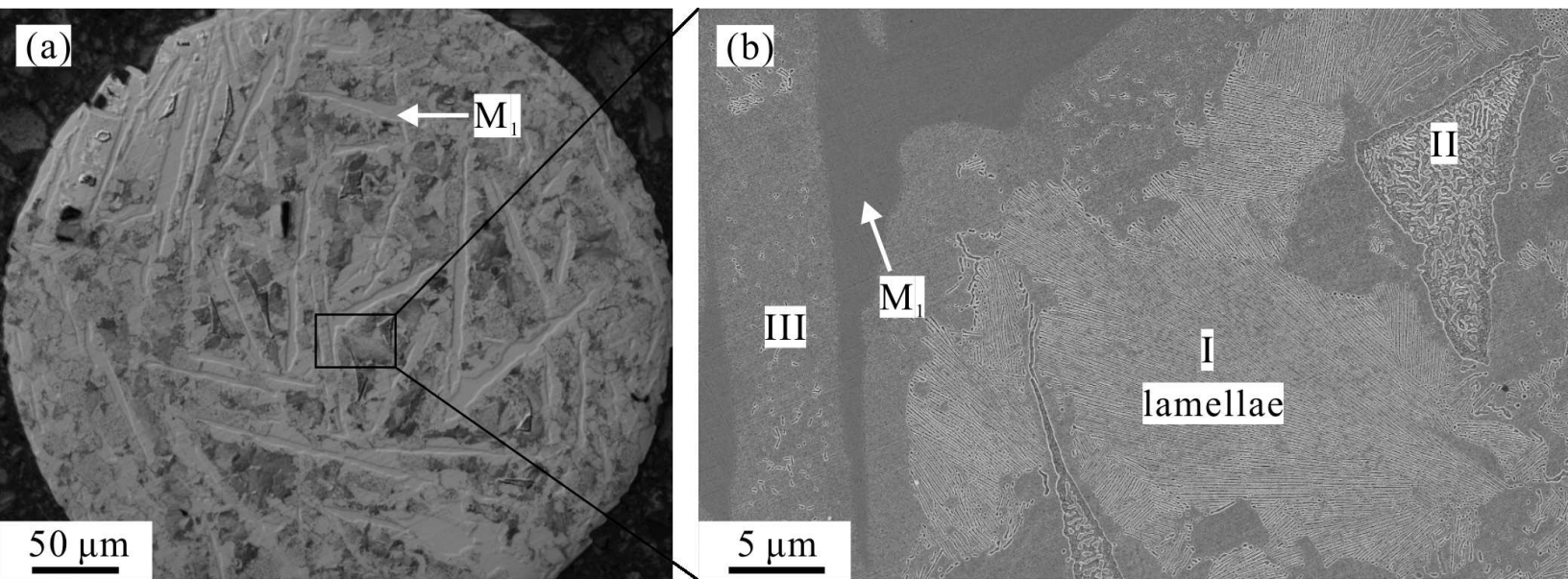


Fig. 6. Micrograph (a) showing the mixed structure of one 300-500 μm droplet, including the single phase M_1 , regular structure I, anomalous eutectic structure II and heteroclitite structure III. Magnified region (b) showing the detailed microstructure highlighted by black square.

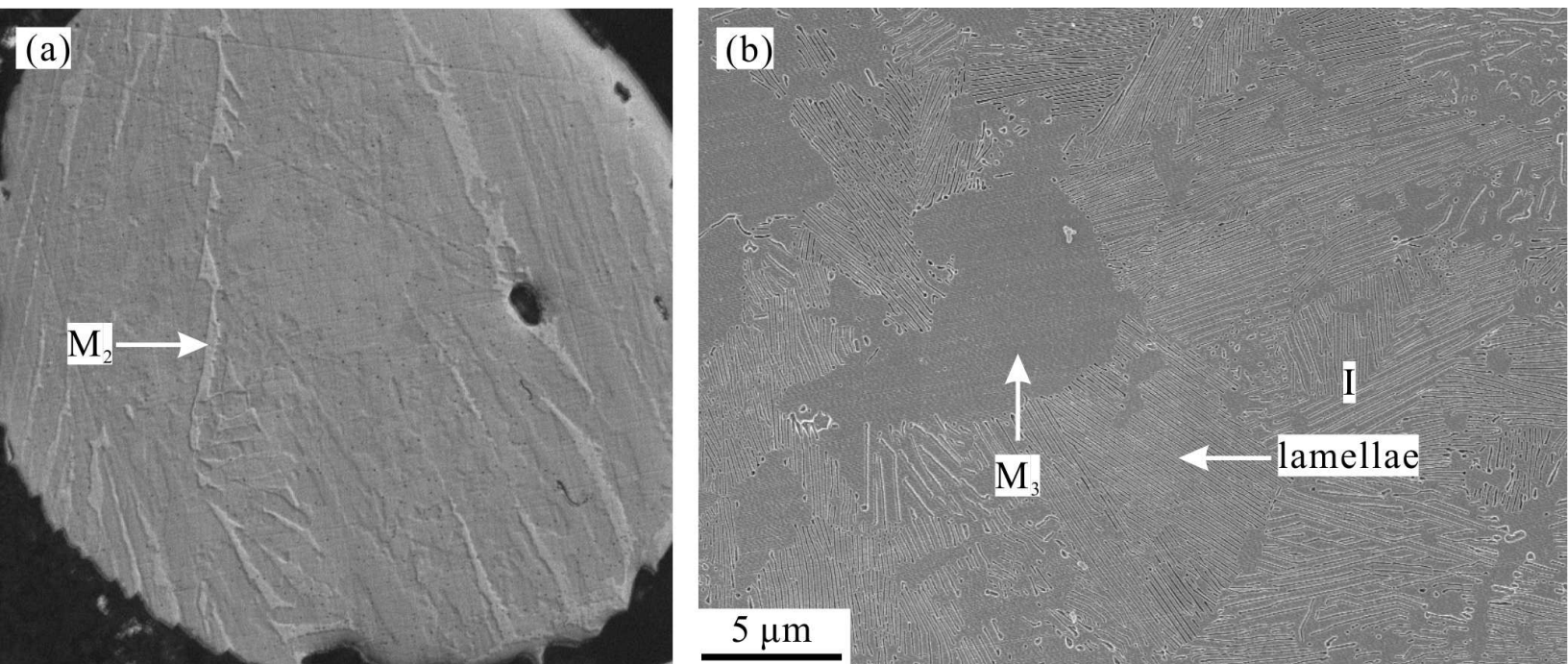


Fig. 7. Micrograph (a) showing the phase M_2 solidified continuously throughout the whole 300-500 μm droplet. Micrograph (b) showing the phase M_3 surrounded by the lamellar structure I. Both phases will be identified by TEM.

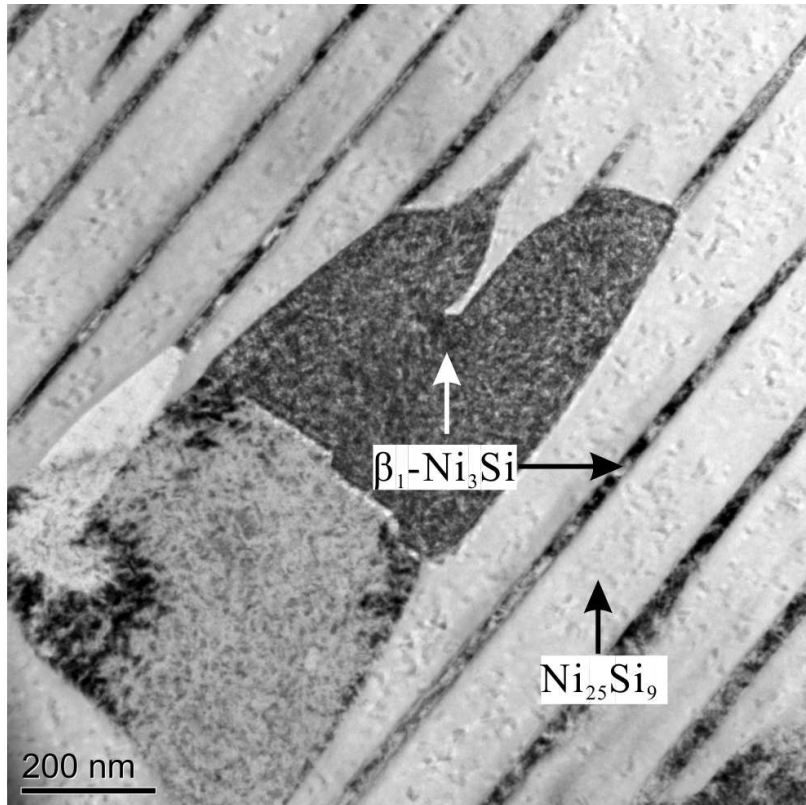


Fig. 8. TEM bright field image showing the regular lamellar structure I. The wide band is identified as the metastable phase Ni₂₅Si₉, while the narrow band and the bulk dark phases are identified as β₁-Ni₃Si.

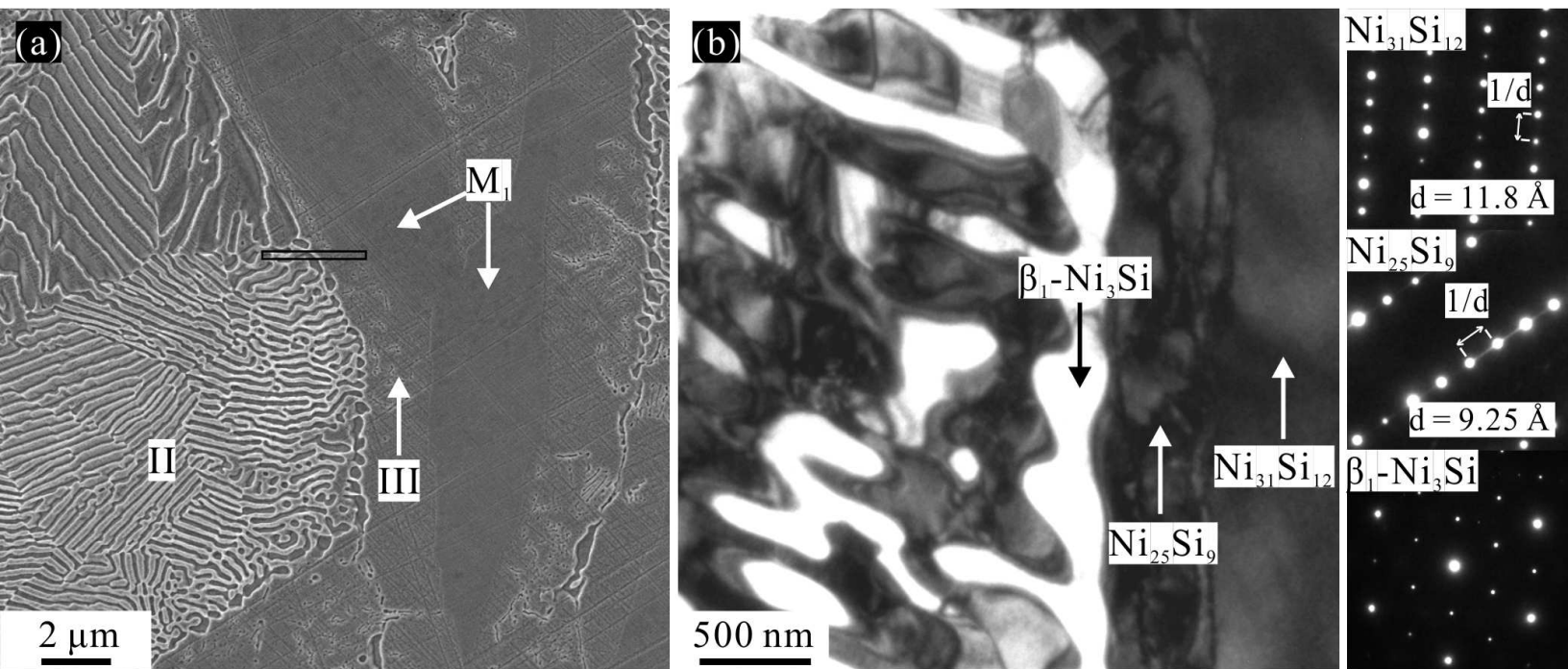


Fig. 9. (a) SEM micrograph showing the structure of one 75-106 μm droplet. (b) The TEM bright field image showing the microstructure of the area highlighted by black square in (a). The single phase M1 is identified as $\gamma\text{-Ni}_3\text{Si}_{12}$, while the eutectic structure consists of $\text{Ni}_{25}\text{Si}_9$ and $\beta_1\text{-Ni}_3\text{Si}$.

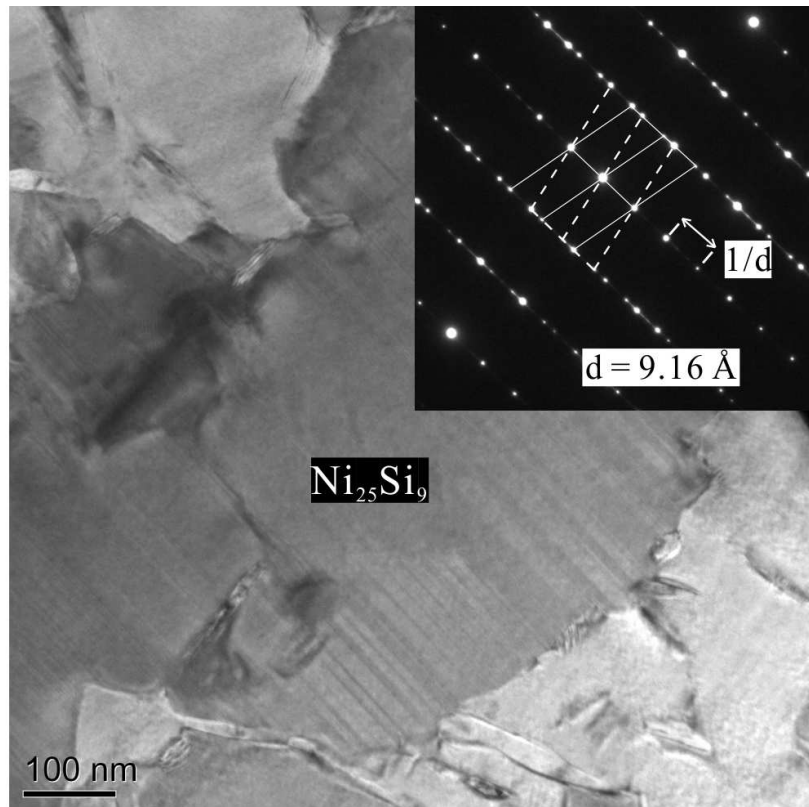


Fig. 10. The TEM bright field image of the heteroclite structure II. The inset is the selected diffraction pattern of the matrix phase, indicating the twinned growth of $\text{Ni}_{25}\text{Si}_9$.

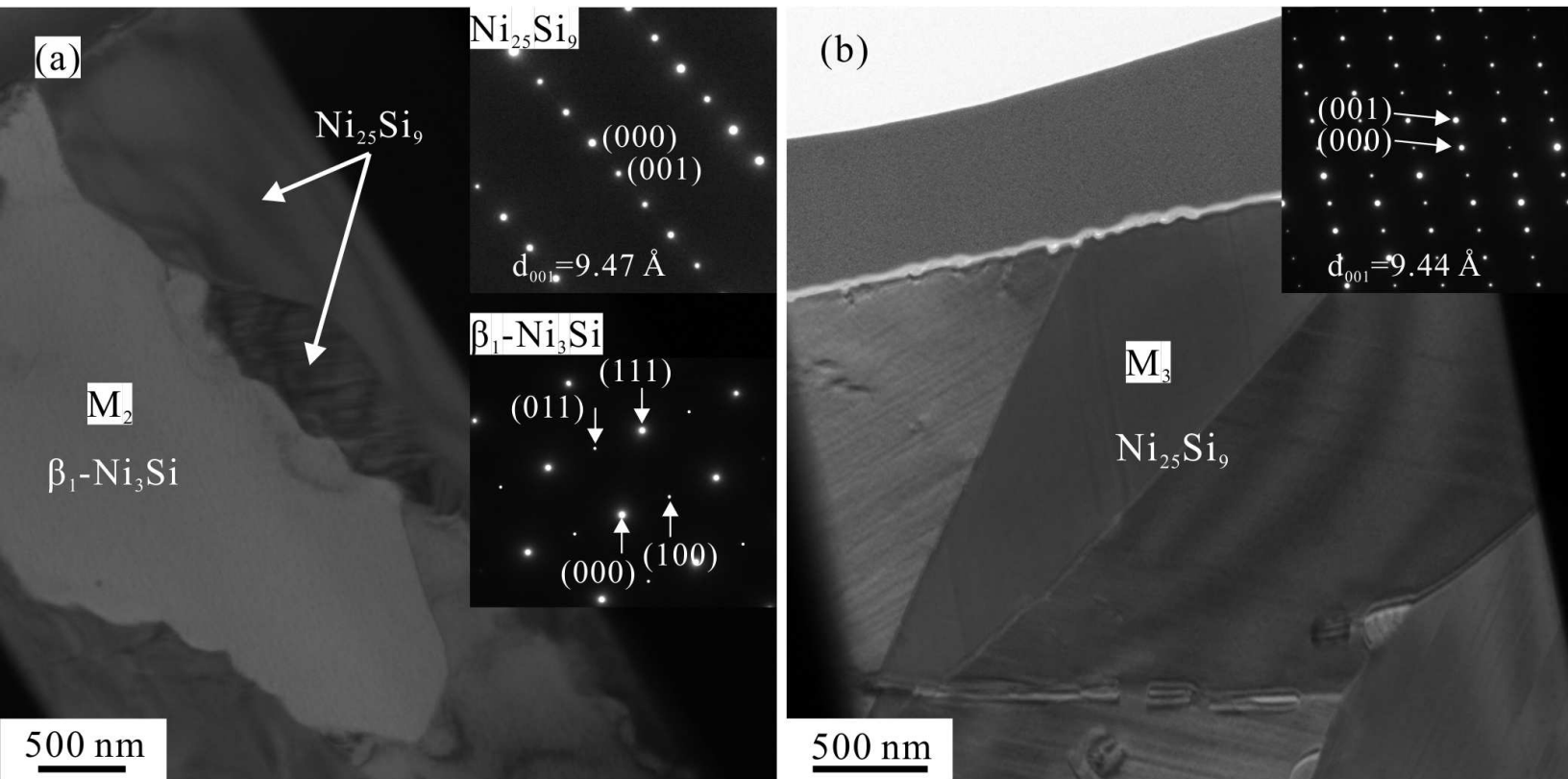


Fig. 11. The TEM images of (a) M₂ phase and (b) M₃ phase, which are identified as β₁-Ni₃Si and Ni₂₅Si₉, respectively. The phase next to β₁-Ni₃Si (M₂) is also the metastable phase Ni₂₅Si₉.

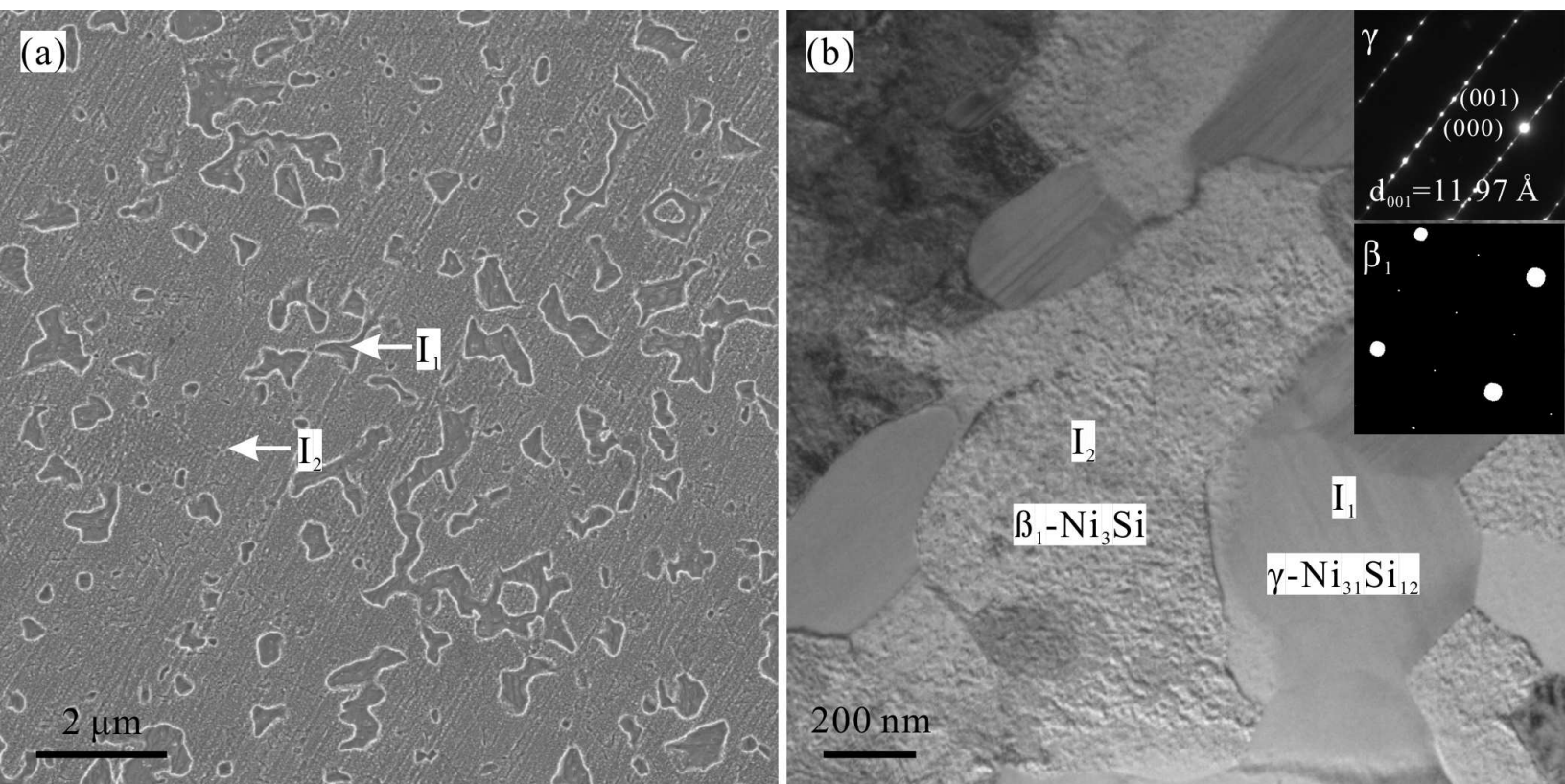


Fig. 12. (a) Micrograph showing the structure of the heat-treated particle (at 867 K (594 °C) for about 30 minutes). The original particle presents the entire heteroclite structure. (b) TEM image showing the structure of heat-treatment sample. The selected-area Diffraction patterns indicate I₁ and I₂ are γ-Ni₃₁Si₁₂ phase and β₁-Ni₃Si phase (matrix).

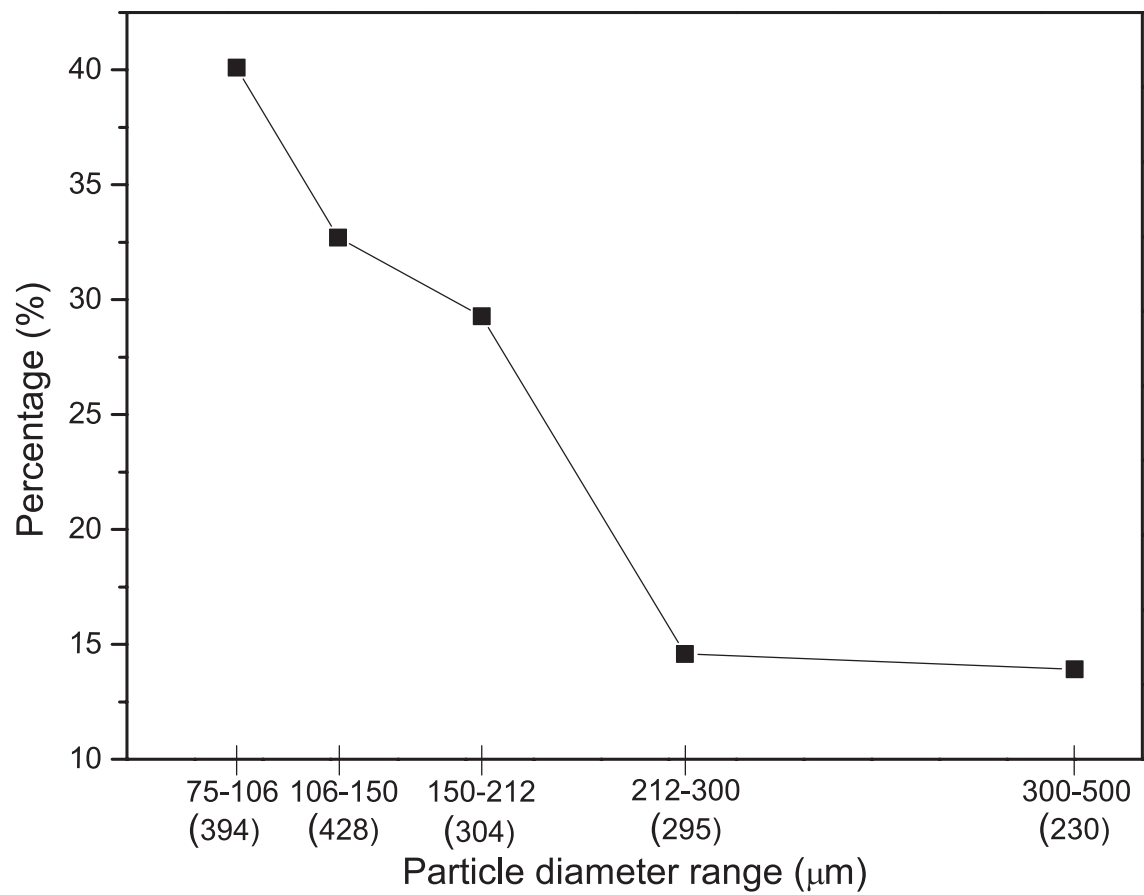


Fig. 13. The fraction of the droplets with the entire heteroclite structure in different particle ranges.