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Crystal growth in undercooled melts of the intermetallic compounds FeSi and CoSi

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Alloy melts of the intermetallic compounds FeSi and CoSi were deeply undercooled using the melt fluxing technique. Crystal-growth velocities were measured as a function of undercooling by a high-speed photosensing infrared device. The experimental results were analyzed in the framework of dendrite growth theories with special emphasis placed on the kinetic interface undercooling. This analysis gives insight into nonequilibrium effects occurring during rapid solidification of undercooled melts of intermetallic compounds due to short-range diffusion-limited dendritic growth.

I. INTRODUCTION

Recent investigations of rapid solidification phenomena in undercooled metallic melts have attracted attention from both theoreticians and experimentalists alike. These investigations provide information about the formation of metastable solids such as supersaturated and disordered states. If a melt can be undercooled by a substantial amount below the melting temperature, great driving forces for crystallization arise leading to rapid solidification of even bulk melts, which, in this case, are slowly cooled. Such experiments are of special interest because they permit direct observation and measurement of the crystal-growth velocities, which in turn determines the physical conditions of the formation of nonequilibrium solid states.

The conditions as underlying in undercooled melts imply an unstable solidification front due to the negative temperature gradient ahead of the solid-liquid interface leading to free dendritic growth. Theories of free dendritic growth in undercooled melts have been developed, which correlate the growth velocity V with the undercooling ΔT and the dendrite tip radius.[1,2] They have been extended for the case of rapid solidification[3,4] to incorporate deviations from local equilibrium at the solidification front due to interface attachment kinetics[5] and, for alloys, due to a velocity-dependent partition coefficient $k(V)$.[6] These theories are able to describe dendrite growth velocities as a function of undercooling without any adjustable parameters.

From the experimental point of view, techniques have been developed to directly measure dendrite growth velocities as a function of undercooling in bulk melts[7,8] undercooled by employing the electromagnetic levitation technique[9] or the melt fluxing method.[10] Measurements on pure Ni and Cu-Ni alloys give experimental evidence that during rapid dendritic growth in undercooled melts deviations from the local equilibrium occur which become progressively more important with increasing undercooling or crystal-growth velocity.[11] In addition, investigations on dilute Ni-B alloys more clearly revealed the importance of such nonequilibrium effects during rapid dendrite growth on the formation of supersaturated solid phases. The results of these experiments indicate a strong increase of the crystal-growth velocities in the vicinity of a critical undercooling where the stability limit of solutal dendrites is reached. This result is explained by solute trapping effects and is interpreted by a transition from diffusion to thermally governed dendrite growth in the vicinity of a critical undercooling.[12]

In addition to the theoretical studies of solute trapping in rapid dendritic solidification of alloys, Boettinger and Aziz recently developed an analogous model to describe trapping of disorder during rapid solidification of intermetallic compounds.[13] Similar to the case of chemical segregation, the formation of a superlattice in intermetallic compounds requires short-range diffusion of atoms. If the growth velocity approaches the speed of atomic diffusion disorder becomes progressively entrapped leading to disordered compounds. Such metastable chemically disordered materials are interesting from a practical point of view, since they are less difficult to machine or forge at room temperature to near net shape. Subsequent annealing would bring out the chemical order and the associated high-temperature properties. Although rapid quenching techniques such as melt-spinning,[14] laser surface resolidification[15,16] and drop tube experiments[17] have yielded chemically disordered structures of intermetallics, no direct measurements of growth velocities in undercooled intermetallic compounds have so far been reported from these experiments.

In the present work, measurements of crystal-growth velocities as a function of undercooling are reported for intermetallic compounds of FeSi and CoSi alloys. These materials were selected for the investigations since they form intermetallics with a congruent melting behavior so that any confusion due to simultaneously occurring solute trapping is excluded. Furthermore, these alloys have an equiatomic composition which would give an order-disorder transition of the second order.[18] This makes the analysis within the disorder trapping model easier. The intermetallic alloys of FeSi and CoSi can be undercooled significantly using the melt fluxing technique. They both form a simple cubic-ordered structure called $B20$ which consists of two sublattices. The experimental results were analyzed within a dendrite growth theory which introduces a kinetic undercooling that depends on an order parameter for the order-disorder tran-

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sition. While an analysis of the FeSi results reveal mainly ordered growth in the entire range of achievable undercooling of $\Delta T = 300$ K, the analysis of the CoSi results may indicate disorder trapping at the largest undercooling of 320 K reached in these experiments.

II. EXPERIMENT

The experiments were accomplished using a glass-flux undercooling facility[19] under a 80-kPa He-20% H_2 atmosphere. Samples of composition $Fe_{50}Si_{50}$ and $Co_{50}Si_{50}$ were alloyed by radio-frequency induction melting from Co, Fe, and Si constituents all of purity better than 99.998%. Each sample had a mass of approximately 1 g and was immersed into a Duran glass slag in an Al_2O_3 crucible. Heating was performed by induction heating of an outer graphite crucible. The absolute temperature was measured by a two color pyrometer at an accuracy of ± 5 K and a measuring frequency of 100 Hz. The recalescence time during solidification was measured by a specially designed infrared photodiode device that has a quartz lens and a S153P photodiode of a sensitive area of 2.8×2.8 mm^2 and a response time of 50 ns. This device was constructed and installed so that the whole image of the sample could be focused onto the sensitive area of the photodiode. Both the pyrometer and the photodiode device were simultaneously coupled to a W+W/SMR-2 transient-signal memory recorder with a sampling rate of 10 MHz.

As the recalescence front was a sharp visible interface between hotter and colder parts of the sample, which swept across the sample surface, the recalescence velocity was taken to a first-order approximation as the ratio of the sample size to the recalescence time. Under such a definition, the measured recalescence velocity showed a rather large scatter. This is since nucleation can take place simultaneously at more than one site and the solidification pathway is unknown. The actual recalescence velocity should therefore be the lower limit of all the different data obtained for a certain undercooling. This corresponds to the cases when a single nucleation event at the periphery of the sample surface takes place, and when the solidification pathway is perpendicular to the direction of observation. This means that a large number of heating and cooling cycles were necessary to get the true physical information. A total of about 100 recalescence events for each sample system were analyzed, and altogether 10 samples were processed. This procedure was verified by calibration measurements on pure Ni using the same arrangement, and comparing the results with those previously obtained from experiments performed in the electromagnetic levitation facility.[7,11] In these experiments the solidification path is very well defined by seeding the nucleation externally using a trigger needle. Unfortunately, this technique is less convenient for FeSi and CoSi alloys because of their high electrical resistivity. Further experimental details of the measurements are given elsewhere.[20] After the undercooling and solidification experiments, each sample was investigated with respect to its composition by energy-dispersive x-ray (EDX) analysis, revealing that the actual concentration deviates less than 0.5 at. % from the nominal concentration.

III. EXPERIMENTAL RESULTS

Figure 1 shows the measured crystal-growth velocity V (dots) as a function of undercooling ΔT of FeSi intermetallic alloy. A continuous increase of V with ΔT is observed up to the largest undercooling of $\Delta T = 300$ K with a maximum velocity of 2.5 m/s. Figure 2 shows the equivalent results obtained for CoSi intermetallic compound. The dependence of the growth velocity V on the undercooling ΔT is similar to that observed for the FeSi alloy. However, at the largest undercoolings ($\Delta T > 300$ K) a steep rise of the growth velocity occurs with maximum growth velocities of nearly 6 m/s. In comparison to the growth velocities measured in pure metals or simple solid solutions,[7,8,11] the growth velocities of the intermetallic compounds are approximately one order of magnitude smaller.

IV. DENDRITIC GROWTH IN MELTS OF INTERMETALLIC COMPOUNDS

For the analysis of the growth behavior we refer to models developed to describe rapid dendritic growth in undercooled melts. According to the Lipton-Kurz-Trivedi (LKT) model,[1,2] the total undercooling is expressed as the sum of different contributions. Under the assumption of local equilibrium at the solid-liquid interface the total undercooling ΔT can be expressed by

$$\Delta T = \Delta T_t + \Delta T_r \ . \tag{1}$$

The constitutional undercooling is neglected since the intermetallic compounds FeSi and CoSi show a congruent melting behavior as observed in the respective

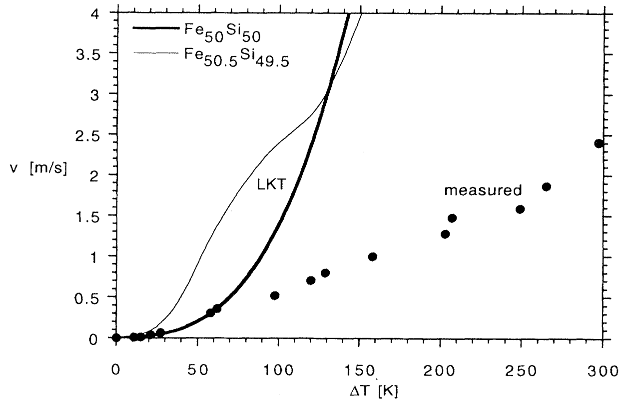

FIG. 1. Crystal-growth velocity V as a function of undercooling ΔT for intermetallic FeSi compound. The dots give the experimental results; the thick solid line corresponds to the predictions of Lipton-Kurz-Trivedi (LKT) theory (Refs. 1 and 2) if local equilibrium at the solid-liquid interface is assumed. For comparison, the thin solid line shows results of calculations if constitutional effects are taken into account due to a slight shift of the composition by 0.5 at. % from the nominal composition.

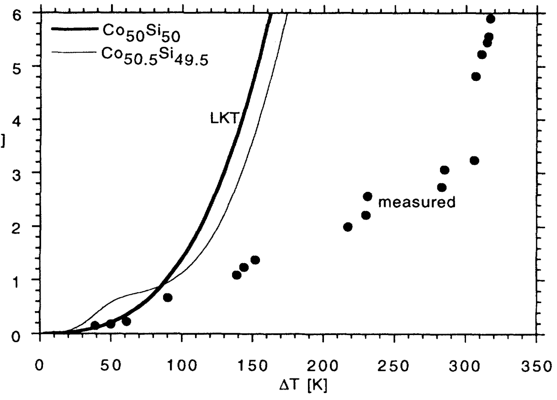

FIG. 2. Crystal-growth velocity V as a function of undercooling ΔT for intermetallic CoSi compound. Notation is the same as in Fig. 1.

temperature-time profile of each heating and cooling cycle. ΔT_t and ΔT_r denote the thermal and the curvature undercooling, respectively. These are given by

$$\Delta T_t = \frac{\Delta H_f}{C_p^l} Iv(P_t) \ , \tag{1a}$$

$$\Delta T_r = 2\frac{\Gamma}{R} \ , \tag{1b}$$

where ΔH_f is the heat of fusion, C_p^l is the specific heat of the undercooled melt, Iv is the Ivantsov function, $P_t = VR/(2a)$ is the thermal Péclet number, R is the dendrite tip radius, a is the thermal diffusivity, $\Gamma = \sigma/\Delta S_f$ is the Gibbs-Thomson coefficient, ΔS_f is the entropy of fusion, and σ is the solid-liquid interface energy.

At large undercoolings or high growth velocities an additional undercooling term has to be included, which describes the kinetic undercooling of the interface $\Delta T_k = T_L - \Delta T_r - T_i$, where T_L is the liquidus temperature of the alloy and T_i is the solid-liquid interface temperature. Following the rate theory of crystal growth[21] the interface undercooling is deduced by calculating the transition rates of atoms going from the liquid to the solid state, R_l and, vice versa, the rate of atoms going from the solid to the liquid state, R_s giving $V = \delta(R_l - R_s)$. The thickness δ of the interface is typically a few interatomic spacings. This yields

$$\begin{aligned} V(T) &= V_c\left[1 - \exp\left[-\frac{\Delta G}{k_B T}\right]\right] \\ &= V_c\left[1 - \exp\left[-\frac{\Delta H_f \Delta T_k}{k_B T T_L}\right]\right] \ . \end{aligned} \tag{1c}$$

ΔG is the Gibbs free-energy difference between the undercooled melt and the solid state and k_B is Boltzmann's constant. In Eq. (1c) the validity of the linear approximation for the Gibb's free-energy difference is assumed, thus $\Delta G = \Delta H_f \ \Delta T/T_L$.[22] In the case that the atomic attachment kinetics at the interface are collision limited, the prefactor V_c corresponds to the speed of sound V_s as an ultimate upper limit of crystal-growth velocity.[23] This means that the attachment of atoms onto the interface is governed by the atomic vibrational frequency $v_0 = k_B T/h$, which is of the order of 10^{13} Hz (h is Planck's constant). This results in an interface undercooling $\Delta T_k \approx V/\mu$ where $\mu = \Delta H_f V_s/(k_B T_L^2)$ is the kinetic growth coefficient. Measurements on pure Ni melts give evidence for collision-limited growth kinetics.[5] On the other hand, growth of a superlattice structure in intermetallic systems is expected to be governed due to short-range atomic diffusion.[24] In this case where the atomic attachment kinetics are controlled by diffusion processes, the prefactor V_c is given by the atomic diffusion speed V_d which is determined by

$$V_d = \delta v_\sigma \exp\left[-\frac{\Delta G_a}{k_B T}\right] \ , \tag{1d}$$

where ΔG_a denotes the activation energy for atomic diffusion. This leads to an interface undercooling ΔT_k being much larger than in the case of collision-limited growth.[25]

Equations (1) give relationships between the undercooling ΔT and the product of V times R in terms of the thermal Péclet number P_t. For a unique determination of V as a function of ΔT the criterion of marginal stability[26] is used which yields an expression for the dendrite tip radius R:

$$R = \frac{\Gamma/\sigma^*}{P_t(\Delta H_f/C_p^l)(1-n)} \tag{2}$$

with

$$n = \frac{1}{\sqrt{1 + 1/\sigma^* P_t^2}} \ ,$$

where $\sigma^* = 1/(4\pi^2)$ is the stability parameter.

Previous measurements of the dendrite growth velocities on undercooled pure metals and simple solid solutions showed that the experimentally determined growth velocity-undercooling relation is well described within dendrite growth theory. Calculations were performed using Eqs. (1) and (2) and assuming that the kinetic interface undercooling ΔT_k is controlled by the conditions of collision-limited atomic attachment kinetics.[11] In the present case of intermetallic compounds it is expected that the interface undercooling is governed by short-range atomic diffusion, since the atoms must sort themselves out onto the various sublattices. In more detail, at lower undercoolings growth should be diffusion limited, while at progressively higher undercoolings (or increased growth velocity) the entrapment of disorder becomes more likely so that a transition from ordered to disordered growth is predicted to occur. This situation is entirely analogous to the entrapment of solute in dilute alloys at high growth velocities as described by the model of solute trapping[5] and experimentally observed in dendrite growth of dilute Ni-B alloys.[12]

To describe a transition from ordered to disordered growth of undercooled intermetallic compounds, we refer to the model developed by Boettinger and Aziz.[13,25] This model gives an expression for the velocity-dependent interface temperature T_i which is dependent on an order parameter η, defined as the concentration x_A^α of alloy component A on sites of sublattice α minus the corresponding concentration $x_A^\beta, \eta = x_A^\alpha - x_A^\beta$, yielding

$$\frac{dT_i}{dV} = -\frac{R_g T_i^2}{\Delta H}\left[\frac{1}{V_s}\frac{f(\eta)}{f(\eta)+g(\eta)} + \frac{1}{V_d}\frac{h(\eta)}{f(\eta)+g(\eta)}\right] . \tag{3}$$

Equation (3) describes the transition from a sluggish interface motion at small growth velocities $V \ll V_d$ to a highly mobile interface at large growth velocities $V \gg V_d$. The functions f, g, and h are defined as follows:

$$f(\eta) = -(M + 1 + (1+\eta) M \ln M) , \tag{3a}$$

$$g(\eta) = -\frac{\eta^2 R_g T_i}{\Delta H}\left[\frac{1+\eta}{\eta}\right] M \ln M \ln\left[\frac{M(1+\eta)}{1-\eta}\right] , \tag{3b}$$

$$h(\eta) = \eta^2 \ln\left[\frac{M(1+\eta)}{1-\eta}\right] , \tag{3c}$$

where $M = \exp(\Omega_1 \eta / R_g T_i)$. R_g is the gas constant and Ω_1 is a thermodynamic parameter for the Gibbs free energy of the solid. This parameter is correlated to the (negative) heat of mixing ΔH_{mix} and the equilibrium long-range order parameter η_e by

$$\Omega_1 = 4\Delta H_{\text{mix}} / (1 + \eta_e^2) . \tag{3d}$$

Equation (3) is valid for intermetallic binary compounds of equiatomic composition, which show a (virtual) second-order transition from an ordered to a disordered state with a transition temperature T_c above the melting temperature T_L. Under this assumption the critical transition temperature T_c and the critical growth velocity V_c for disorder trapping are given by

$$T_c = \frac{\Omega_1}{2R_g} , \tag{4a}$$

$$V_c = V_d\left[\frac{T_c}{T_L} - 1\right] . \tag{4b}$$

As can be seen from Eq. (4) the higher the value of T_c the larger the critical velocity at which disorder trapping occurs. Since T_c scales with the heat of mixing one expects low critical velocities in the case of alloys showing a small ΔH_{mix}.

V. ANALYSIS OF THE EXPERIMENTAL RESULTS

The analysis of the experimental results obtained from the measurements on the FeSi and CoSi intermetallic compounds is based upon the application of Eqs. (1)–(4). The assumptions of Eq. (3) are fulfilled since the investigated alloys are equiatomic in composition.

A. The intermetallic compound FeSi

For the analysis of the experimental results we calculate the interface temperature as a function of growth velocity. The interface temperature T_i is obtained from

$$T_i = T_L - \Delta T_r - \Delta T_k . \tag{5}$$

The curvature undercooling ΔT_r is determined by applying Eq. (1b) and using Eq. (2) to calculate the dendrite tip radius R. In order to determine the kinetic undercooling ΔT_k, first the growth velocity is calculated by assuming local equilibrium at the interface and using Eqs. (1) and (2). The results of these calculations are given by the thick solid line in Fig. 1. It is apparent that the assumption of local equilibrium at the solid-liquid interface leads to a large overestimation of the growth velocities in comparison to the experimental results. If it is assumed that the interface attachment kinetics are controlled by collision-limited growth, only a small kinetic undercooling $\Delta T_k < 1$ K results, which does not explain the experimental findings. A possible influence of constitutional effects due to a slight shift of the composition from the nominal concentration was tested. The $V(\Delta T)$ relation was calculated taking into account a constitutional undercooling and constitutional effects in the marginal stability analysis. To do this the same formalism is applied as was used in Ref. 12. The results of these calculations are represented by the thin lines in Fig. 1 using the values of the thermophysical parameters given in Table I. It is obvious that constitutional effects due to a change in the composition within 1 at. % corresponding to the uncertainty of the EDX measurements cannot explain the deviation of the calculated results from the experimental behavior. This finding is in agreement with a microstructure analysis of the $Fe_{50}Si_{50}$ sample and a reference sample made of $Fe_{54}Si_{46}$. While in the latter case segregation in the grain boundaries is clearly visible, no segregation could be detected in the former case.

Therefore, as previously supposed, a large interface undercooling should occur due to short-range diffusion-

TABLE I. Numerical values of thermophysical properties used for the analysis of the growth velocity measurements. The values marked by an asterix (*) are taken from Refs. 30 and 31. The slope of the liquidus line, m_l, and the equilibrium partition coefficients, k_E, for alloys deviating in concentrations by 0.5 at. % from the nominal composition were calculated from the phase diagrams given in Ref. 32. The Gibbs-Thomson coefficient Γ is determined on the basis of calculations of the interface energy within the negentropic model 33. The remaining parameters are estimated in such a way to give a best fit to the experimental results.

Parameter	Dimension	FeSi	CoSi
ΔH_f	kJ/mol	35.2*	35.2
C_p^l	J/(K mol)	42*	42
T_L	K	1683*	1693*
a	m^2/s	5×10^{-6}*	5×10^{-6}*
Γ	Km	2.8×10^{-7}	2.8×10^{-7}
V_s	m/s	3000*	3000*
V_d	m/s	15	5
ΔH_{mix}	kJ/mol	−42.2*	−19.8
m_l	K/at. %	−10	−10
k_E		0.05	0.05

controlled growth at the interface. The actual kinetic undercooling is inferred from the difference of the measured data and of the calculated curve $V = V(\Delta T)$ under the assumption of local equilibrium (thick solid line in Fig. 1) at the interface. To do so the experimental results were fitted by a power law of the second order. The difference between this fit and the curve calculated within the LKT approach gives the kinetic undercooling from which the interface temperature can be inferred. The results are shown in Fig. 3 where the interface temperature T_i is plotted versus the growth velocity V. The curvature undercooling ΔT_r is less than a few percent of the kinetic interface undercooling ΔT_k which is represented by the difference between the $T_L - \Delta T_r$ curve and the interface temperature T_i. The steep slope of the interface temperature-velocity curve indicates a sluggish interface movement due to short-range diffusion-limited growth. In this velocity regime the melt solidifies as an ordered superlattice structure without the occurrence of significant disorder trapping.

Using the data given in Table I and applying Eqs. (3) and (4) the velocity dependence of the order parameter η is calculated, the results of which are plotted in Fig. 4. An appropriate value of the equilibrium order parameter at a velocity $V=0$ m/s, $\eta=0.9$ was selected.[27] A value close to 1 is verified by the observation that the velocity-undercooling results at small growth velocities can be well described employing Eqs. (1)–(4) and using $\eta=0.9$. Even in the case where η is changed by ± 0.1 the modifications to the calculated results are within the uncertainty of the measurements. The velocity-dependent order parameter is seen to slightly decrease with increasing growth velocity. In particular, no sharp drop of the order parameter can be observed. This indicates that the maximum measured growth velocities of about 3 m/s are not sufficient to cause significant disorder trapping in the FeSi intermetallic compound. The order parameter decreases from the equilibrium value of $\eta=0.9$ to about 0.75 at the maximum growth velocity of 3 m/s. The analysis suggests that the critical velocity for disorder trapping in FeSi intermetallic compound is much higher than 3 m/s. The value given by Eq. (4b) is predicted to be 35 m/s.

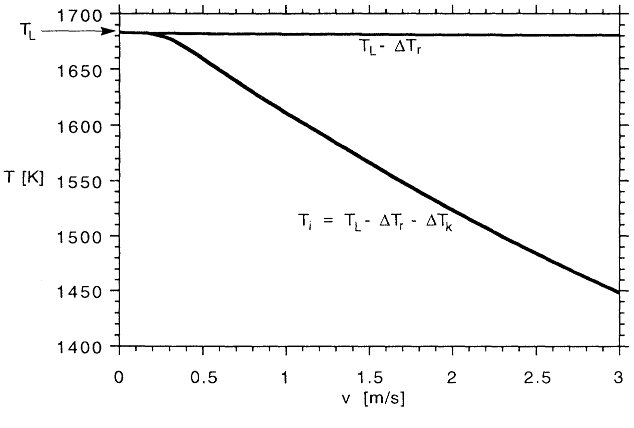

FIG. 3. The interface temperature T_i as a function of the growth velocity V for FeSi. The line labeled $T_L - \Delta T_r$ gives the equilibrium interface temperature; its slope is very small indicating a negligible contribution of the curvature undercooling ΔT_r in comparison to the kinetic undercooling $\Delta T_k = T_L - \Delta T_r - T_i$.

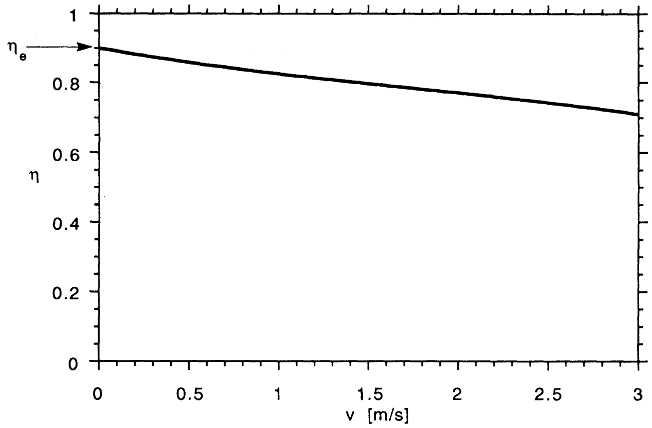

FIG. 4. The order parameter η as a function of the growth velocity V for FeSi. The order parameter is obtained from the results shown in Fig. 3 and by applying the model of disorder trapping by Boettinger and Aziz (Ref. 13). It decreases slightly from the equilibrium value of 0.90 to 0.75 at the largest growth velocity measured.

B. The intermetallic compound CoSi

For the analysis of the results of the measurements on CoSi the same procedure was applied as for FeSi. Calculations of the velocities as a function of undercooling assuming local equilibrium at the solid-liquid interface [using Eqs. (1) and (2)], similarly leads to an overestimation of the growth velocities. The predictions given by the thick solid line in Fig. 2 also deviate from the experimental results as with the case of the FeSi alloy. Also the interface undercooling $\Delta T_k < 2$ K as calculated under the assumption of collision-limited growth is not able to describe the experimental results. A sudden change of the temperature characteristics of the measured $V(\Delta T)$ relation is found at a critical undercooling of approximately 300 K or at a critical velocity of about 4 m/s. At undercoolings larger than this critical undercooling the velocity rises sharply with a temperature dependence as do the calculations which use the assumption of local equilibrium at the solidification front. A similar behavior has been reported for dilute Ni-B alloys in which this sharp increase of the growth velocity at a critical undercooling has been attributed to the onset of solute trapping.[12] However, in the present case of the intermetallic CoSi alloy, such a behavior cannot be explained by solute trapping since this alloy shows congruent melting. Similar to the case of FeSi, constitutional effects due to deviations from the nominal composition can be excluded as demonstrated by the thin solid line in Fig. 2. It can be seen that this does not lead to an improvement of the description of the experimental results. It follows that constitutional effects are not present. For a further analysis it is therefore assumed that the transition at the critical undercooling of 300 K might be caused by the onset of disorder trapping.

Figure 5 shows the interface temperature of CoSi alloy as a function of the growth velocity. As in the case of the FeSi alloy the curvature undercooling is negligible in comparison with the kinetic interface undercooling. The latter is obtained from the difference between the $T_L - \Delta T_r$ curve and the measured data. The interface temperature T_i decreases continuously with growth velocity until a growth velocity of about 4 m/s is reached. At higher values of v the interface temperature shows only a slight dependence on v. This transition is indicative of a change from a sluggish interface motion at small growth velocities to a highly mobile interface at large growth velocities.

If the change of the growth characteristics at a velocity of 4 m/s is attributed to the onset of disorder trapping the critical velocity of disorder trapping is assumed to be of the order of 4 m/s. Using Eq. (4b) and assuming a typical value for the atomic diffusion speed $V_d \approx 5$ m/s, the critical temperature T_c for the order-disorder transition is estimated to be 1.80 T_L. In such a case where the critical temperature T_c is not too far above the melting temperature, the equilibrium order parameter η_e at the melting temperature might be of the order of 0.75.[27] This is verified by the observation that the velocity-undercooling results at low growth velocities are well described with Eqs. (1)–(4) and using this value of the equilibrium order parameter. By taking this value as a reference, Fig. 6 shows the dependence of the order parameter η on the growth velocity. This relation is obtained from the results given in Fig. 5 and by applying Eqs. (3). The order parameter decreases from its equilibrium value of $\eta_e = 0.75$ at $V = 0$ m/s to $\eta = 0$ at a velocity $V \approx 4$ m/s. This means that at such a velocity disorder trapping sets in leading to a disordered structure of the solidified intermetallic compound.

Comparing the results obtained from the analysis of the data of FeSi and CoSi it seems evident that the critical velocity for the onset of disorder trapping in FeSi is much higher than that for CoSi. Obviously, the maximum undercooling, $\Delta T = 300$ K, achieved in the case of the FeSi alloy, was not sufficient to generate growth velocities necessary for the onset of disorder trapping. In the case of the CoSi alloy, a maximum undercooling of $\Delta T = 320$ K has been reached causing maximum growth velocities which are a factor of 2 times larger than those of the FeSi alloy. The present analysis for the CoSi alloy is based upon the assumption that the experimentally observed change in the temperature characteristics of $V(\Delta T)$ at $\Delta T \approx 300$ K or at $V \approx 4$ m/s corresponds to the onset of disorder trapping. This also implies according to Eq. (4a) that the enthalpy of mixing should be a factor of about 2 and the atomic diffusive speed a factor of about 3 times smaller for CoSi than for FeSi. Whereas a measured value for the enthalpy of mixing is reported for FeSi, no value for ΔH_{mix} is known for CoSi. Also, to the best of our knowledge, no data of the atomic diffusion velocities of Fe and Co in liquid Si are available yet in the literature. The numerical values of these parameters were chosen such that the experimental results of the velocity-undercooling measurements could be described within the framework of the models of dendritic solidification incorporating nonequilibrium effects due to disorder trapping.

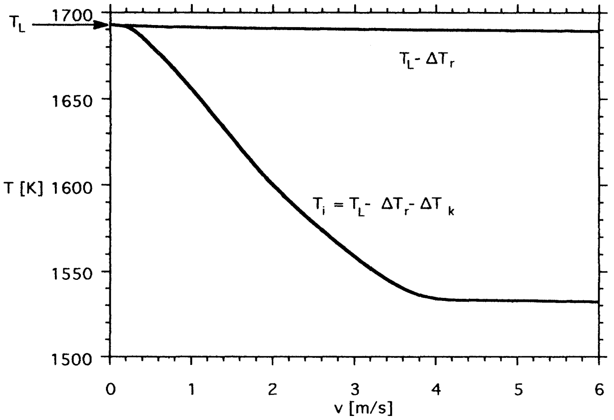

FIG. 5. The interface temperature T_i as a function of the growth velocity V for CoSi; it decreases with increasing velocity similar to FeSi, however, in contrast to FeSi, T_i levels off once a critical velocity of 4 m/s is approached.

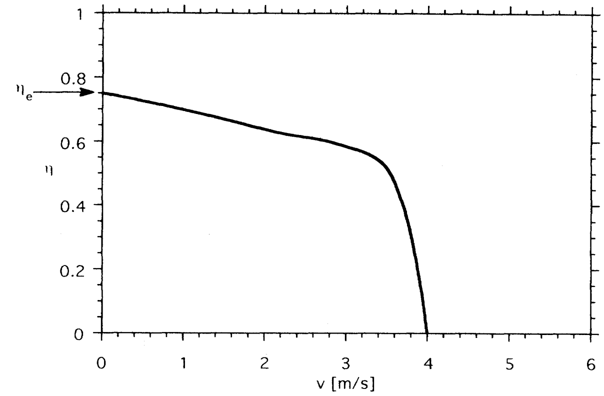

FIG. 6. The order parameter η as a function of the growth velocity V for CoSi. η shows a stronger dependence on V in comparison to FeSi and approaches zero at velocities $V > 4$ m/s.

To support the assumption that the break in the velocity-undercooling relationship of the Co-Si sample can be attributed to an onset of disorder trapping, it would be important to detect antiphase domain boundaries in samples undercooled to more than the critical undercooling at $\Delta T = 300$ K. The presence of such antiphase domains boundaries can be taken as an evidence of disorder trapping.[16] Unfortunately, there are two reasons which make such an analysis for the undercooled CoSi sample extremely difficult. First, the $B20$ crystal structure does not allow the clear distinction between superlattice and fundamental diffraction patterns. Second, the samples are slowly cooled after solidification so that primary formed antiphase domains may easily be destroyed by coarsening.

VI. SUMMARY AND CONCLUSIONS

The present work reports measurements of the growth velocity as a function of undercooling for melts of the intermetallic compounds of FeSi and CoSi. The experimental results were analyzed within current theories of dendritic growth. The analysis leads to the conclusion that a large kinetic interface undercooling is necessary to describe the results. Such a large interface undercooling is explained by short-range diffusion-limited attachment kinetics at the solidification front which are necessary to sort the atoms themselves out onto the various sublattices of the intermetallic alloys. The model of disorder trapping by Boettinger and Aziz[13] is used to deduce from the interface undercooling-velocity relation the dependence of the order parameter on the solidification velocity. For FeSi intermetallic compound only a weak dependence of the order parameter on the solidification velocity is found. In contrast to this, the analysis of the results for CoSi may suggest the onset of disorder trapping at a velocity of 4 m/s that leads to a sharp decrease of the order parameter from its equilibrium value of $\eta_e \approx 0.75$ to $\eta = 0$. Independent measurements of the enthalpy of mixing by, e.g., levitation calorimetry[28] and reliable values for the atomic diffusion speed investigated by, e.g., laser surface resolidification experiments in combination with transient electrical resistivity measurements[29] would allow a verification of the results in the present analysis.

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