Kinetics of the Allotropic hcp-fcc Phase Transformation in Cobalt

Rico Bauer, Eric A. Jaegle, Wolfgang Baumann, Eric Jan Mittemeijer

To cite this version:
Rico Bauer, Eric A. Jaegle, Wolfgang Baumann, Eric Jan Mittemeijer. Kinetics of the Allotropic hcp-fcc Phase Transformation in Cobalt. Philosophical Magazine, Taylor & Francis, 2010, 91 (03), pp.437-457. 10.1080/14786435.2010.525541. hal-00651157

HAL Id: hal-00651157
https://hal.archives-ouvertes.fr/hal-00651157
Submitted on 13 Dec 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
## Kinetics of the Allotropic hcp-fcc Phase Transformation in Cobalt

| **Journal**               | Philosophical Magazine & Philosophical Magazine Letters |
|--------------------------|--------------------------------------------------------|
| **Manuscript ID**        | TPHM-10-Aug-0390.R1                                    |
| **Journal Selection**    | Philosophical Magazine                                 |
| **Date Submitted by the Author** | 15-Sep-2010                          |
| **Complete List of Authors** | Bauer, Rico; University of Stuttgart, Institute for Materials Science 
|                           | Jaegle, Eric; Max Planck Institute for Metals Research, Prof. Dr Ir. E.J. Mittemeijer 
|                           | Baumann, Wolfgang; Max Planck Institute for Metals Research, Prof. Dr Ir. E.J. Mittemeijer 
|                           | Mittemeijer, Eric Jan; University of Stuttgart, Institute for Materials Science; Max Planck Institute for Metals Research, Prof. Dr Ir. E.J. Mittemeijer |
| **Keywords**             | phase transformations, kinetics, modelling, calorimetry |
| **Keywords (user supplied)** | Cobalt, allotropic transformations                     |
Kinetics of the Allotropic hcp-fcc Phase Transformation in Cobalt

Rico Bauer, a Eric Aime Jägle, b,* Wolfgang Baumann b and Eric Jan Mittemeijer a,b

a Institute for Materials Science, University of Stuttgart, Heisenbergstr. 3, 70569 Stuttgart, Germany
b Max Planck Institute for Metals Research, Heisenbergstr. 3, 70569 Stuttgart, Germany
* Corresponding author: E. A. Jägle

Max Planck Institute for Metals Research, Heisenbergstr. 3, 70569 Stuttgart, Germany, Phone +49 (0) 711 689 3316; Fax +49 (0) 711 689 3312; email: e.jaegle@mf.mpg.de

Number words: 7709
Kinetics of the Allotropic hcp-fcc Phase Transformation in Cobalt

The allotropic, martensitic phase transformation hcp→fcc in cobalt was investigated by differential scanning calorimetry (DSC) upon isochronal annealing at heating rates in the range from 10 K min⁻¹ to 40 K min⁻¹. The microstructural evolution was traced by light optical microscopy (LM) and X-ray diffractometry (XRD). The kinetics of the phase transformation from hcp to fcc Co upon isochronal annealing was described on the basis of a modular phase transformation model. Appropriate model descriptions for athermal nucleation and thermally activated, anisotropic interface controlled growth tailored to the martensitic phase transformation of Co were implemented into the modular model. Fitting of this model of phase transformation kinetics to simultaneously all isochronal DSC runs yielded values for the energy of the interface separating the hcp and fcc Co phase and the activation energy for growth.

Keywords: Cobalt; Allotropy; Calorimetry; Transformation kinetics; Modeling
1 Introduction

Pure cobalt exhibits an allotropic phase transformation at the equilibrium temperature $T_0$ (at constant pressure) with the hcp modification as low temperature phase and the fcc modification as high temperature phase. This allotropic transformation shows characteristics of a martensitic transformation [1, 2]: the transformation needs no diffusion and composition change, has a distinct athermal nucleation nature leading to spontaneous initiation of the reaction upon reaching the “martensite” start temperature $M_S$ upon cooling or the “austenite” start temperature $A_S$ upon heating.

Many studies on the mechanism and microstructural evolution associated with the allotropic phase transformation in Co have been performed (e. g. see Refs. 1 - 17), providing controversial or inconclusive results on a number of aspects: The equilibrium temperature and its uncertainty as given in Ref. 4, $T_0 = 690\pm 7$ K (at 1 atm), covers the range of most of the available literature data [2, 9, 11, 18], based on calculations or determined experimentally, taken as average of the “austenite” and “martensite” start temperatures, measured by X-ray diffractometry, magnetometry, dilatometry or calorimetry. Values for the martensite start temperature $M_S$ range from 692 K to 661 K and for the austenite start temperature $A_S$ range from 694 K to 720 K [2, 7, 10]. The difference between the start temperatures for the $fcc\rightarrow hcp$ transformation ($M_S$ temperature) and the $hcp\rightarrow fcc$ transformation ($A_S$ temperature) is called (here) “temperature hysteresis”. Values for the enthalpy of transformation, $\Delta H_{hcp\rightarrow fcc}$, range from 377 to 464 J mol$^{-1}$ [1, 2, 9, 11, 18] and some studies indicate differences upon heating and cooling [10, 15]. The diversity of these results appears to depend on the specimen shape (thin layer [6, 16, 17], powder [3, 5, 12], sheet [8, 10, 13, 15] and rod [1, 3, 5, 7]), the specimen size [10, 15], the state of stress [7, 12] and the (type of) thermal treatment [1, 3 - 8, 10, 12, 15].

It appears that depending on the initial microstructure and experimental conditions (as heating/cooling rate) a significant number of $hcp\rightarrow fcc$ transformation cycles must be passed
through in order to establish reproducible characteristics of the \( hcp \rightarrow fcc \) transformation (see Refs. 1, 2, 5, 10, 15, 19 and, in particular, results of this study presented in section 4). This may contribute to the discrepancies apparent from the literature cited above.

A full, quantitative, description of the kinetics of the allotropic transformation in Co was not presented until now. The present paper for the first time provides such a model description of the allotropic, martensitic transformation kinetics of Co, departing from a general modular model of phase-transformation kinetics composed of separate modes of nucleation, growth and impingement [20, 21], thereby incorporating an athermal nucleation mode as proposed in Ref. 19, interface-controlled growth and anisotropic impingement. This approach was recently applied successfully by our group to the polymorphic transformation of Laves phases [22].

The present paper focuses on the \( hcp \rightarrow fcc \) phase transformation using “stabilized” specimens (i.e. after a number of preceding transformation cycles). Isochronal annealing experiments (i.e. experiments using a constant heating/cooling rate) in a fixed temperature range using Differential Scanning Calorimetry, DSC, were performed. The resulting enthalpy changes as function of time and heating rate were interpreted quantitatively using the modular phase transformation model.

## 2 Theoretical Background of Transformation Kinetics

Solid state phase transformations can take place as soon as the hitherto existing phase is not stable anymore; i.e. a thermodynamic driving force can be indicated. Such a phase transformation can be realized in different ways. In general a phase transformation can be subdivided into three (overlapping) steps: nucleation, growth and impingement. This type of modular approach has been described in [20, 23] (see, especially, the review in Ref. 21) and has been applied successfully to a variety of phase transformations: crystallization of amorphous metal alloys [24 - 29], the austenite-ferrite transformation in Fe-based alloys [30 - 32] and the polytypic transformations of Laves phases [22].
Assuming, hypothetically, that each individual product particle, emanating from a successful nucleation process, grows into an infinitely large parent phase, in the absence of other product particles, the so-called extended volume, $V_e$, given by the sum of the volumes of all these (hypothetical) particles, can be calculated. In a second step the extended transformed fraction, $x_e$ ($= V_e / V_S$; with $V_S$ as the volume of the specimen), has to be corrected for (hard) impingement to obtain the real transformed fraction, $f$, by adopting a certain impingement mode. In the following, after discussing the hcp↔fcc transformation mechanism, nucleation, growth and impingement modes relevant for the hcp↔fcc transformation are indicated briefly.

### 2.1 The hcp↔fcc Transformation Mechanism

The dislocation (line) energy of a so-called perfect dislocation can be reduced by dissociation into two Shockley partial dislocations inducing a stacking fault (SF) in-between both partials, with the stacking fault energy (SFE) $\sigma$. The width of the dissociated partial dislocations is given by the balance of the elastic repulsion force, forcing the dissociation, and the stacking fault energy, $\sigma$, opposing the dissociation: dissociated (perfect) dislocations are a basic component of the microstructure [33].

The transformation of an fcc (ABCABC… stacking sequence) into an hcp (ABABAB… stacking sequence) crystal structure, and vice versa, can be realized by the motion of Shockley partial (SP) dislocations, with Burgers vectors, of type $1/6\{11\bar{2}\}$, on every second closest packed plane [6, 19].

(insert here Figure 1)

This process can be called “ordered glide” as an ordered array of Shockley partials is required for the phase transformation. So this ordered array of $x$ partials transforms a region of thickness $2x$ closest packed layers. The transformation $fcc\rightarrow hcp$ occurs by dissociation of the perfect dislocations and the transformation $hcp\rightarrow fcc$ by association of the SPs (see FIG. 1). Studies of the
microstructural evolution upon thermal (transformation) cycling showed that such ordered dislocation arrangements evolve indeed [6], establishing, by the “back and forth” movement of the same partial dislocations, the reversible $\text{hcp} \leftrightarrow \text{fcc}$ transformation with preservation of the orientation, in the specimen frame of reference, of the $\text{hcp}$ and $\text{fcc}$ crystals, as validated for Co [1].

Each SP can be associated with one of six Burgers vectors of type $1/6 \langle 1 \overline{1} 2 \rangle$ on a closest packed plane leading, upon glide of the SP, to a microscopic shear of the lattice (see top part in FIG. 2). This shear can be nullified (no add up of microscopic to macroscopic shear) by the summation of a set of three successive dislocations in the ordered array of SPs, with Burgers vectors such that $\vec{b}_1 + \vec{b}_2 + \vec{b}_3 = 0$ (see bottom left part in FIG. 2). If $\vec{b}_1 + \vec{b}_2 + \vec{b}_3 \neq 0$, macroscopic shear evolves* (see bottom right part in FIG. 2 where the extreme case, all SPs have same $\vec{b}$, is shown). However, it is usually assumed [13, 14] that microscopic shear cancels out over short distances and therefore the contribution of macroscopic shear to the phase transformation (kinetics) is considered to be negligible in this paper.

*(insert here Figure 2)

Irrespective of the micro-/macroscopic shear discussed above, the allotropic transformation in cobalt is associated with a macroscopic distortion due to the change of the atomic distances. This macroscopic distortion for the $\text{fcc} \rightarrow \text{hcp}$ transformation is $+0.021\%$ parallel to and $-0.242\%$ perpendicular to the closest packed plane [13].

The $\text{hcp}$ crystal lattice has only one closest packed set of $\{0001\}$ planes; the $\text{fcc}$ crystal lattice has four equivalent sets of closest packed $\{111\}$ planes. Upon thermal cycling the dislocation structure is (re)arranged, from any initial state, such, that only one single set of $\{111\}_{\text{fcc}}$ planes is active and parallel to $\{0001\}_{\text{hcp}}$ (further see section 6.1).

* Note that for polymorphic Laves-phase transformations such macroscopic shear is impossible because of the glide of synchro-Shockley partial dislocation dipoles [22].
2.2 Nucleation

The thermodynamic model for nucleation must be compatible with the mechanism for the $hcp\leftrightarrow fcc$ transformation by glide of an ordered array of Shockley partial dislocations (cf. section 2.1). The model presented here is derived from an earlier description of nucleation of the martensitic $fcc\rightarrow hcp$ transformation in metals by dissociation of perfect dislocations [19].

Consider the periodically arranged array of perfect dislocations in an $fcc$ crystal as shown in FIG. 1 and FIG. 3. The $fcc\rightarrow hcp$ phase transformation is performed by glide of the periodically arranged Shockley partial dislocations through the crystal lattice (see section 2.1)

(insert here Figure 3)

Initiation of an $fcc\rightarrow hcp$ transformation requires dissociation of the array of perfect dislocations into two arrays of Shockley partial dislocations. The region in between these two arrays can be described as a stacking faulted region (with reference to the parent structure) or as transformed region (exhibiting the product, $hcp$ crystal structure). As long as $fcc$ is the stable phase, the dissociation is limited by the relatively high energy (with reference to the parent phase) of the faulted structure lying between the two arrays of Shockley partial dislocations. This is no longer the case if the $hcp$ phase becomes the stable phase, i.e. by passing the $hcp-fcc$ phase equilibrium temperature $T_0$ upon (isochronal) cooling from the $fcc$ phase field.

The region between the two separated arrays of Shockley partial dislocations can be considered as two second-phase ($hcp$) particles each having the volume $V$ and the interfacial area $S$. The total Gibbs energy change $\Delta G$ associated with the formation of this second phase particle can be given as:

$$\Delta G = V(\Delta G_v^{ch} + E_v^{sup}) + S \sigma \tag{1}$$
where $\Delta G_{ch}^{\text{ch}} \left( = \frac{\Delta G_{m}^{\text{ch}}}{V_m} \right)$ is the chemical Gibbs energy difference per mole of atoms between product phase and parent phase and $V_m$ is the molar volume, is the chemical Gibbs energy difference between product phase and parent phase per unit volume, $E_{\text{str}}^{\text{ch}} \left( = \frac{E_{m}^{\text{str}}}{V_m} \right)$ is the elastic strain energy per mole of atoms) is the elastic strain energy per unit volume and $\sigma$ is the particle/matrix interface energy per unit area. For small overheating/undercooling, i.e. in the vicinity of the equilibrium phase-transformation temperature $T_0$, the chemical Gibbs-energy change per mole of atoms $\Delta G_{m}^{\text{ch}}$ can be approximately given as:

$$\Delta G_{m}^{\text{ch}} \approx \frac{\Delta H_{\text{hcp} \rightarrow \text{fcc}}}{T_0} \left( T_0 - T \right) = \frac{\Delta H_{\text{hcp} \rightarrow \text{fcc}}}{T_0} \Delta T \quad (2)$$

with $\Delta H_{\text{hcp} \rightarrow \text{fcc}}$ as the molar enthalpy of transformation ($\text{fcc} \rightarrow \text{hcp} : \Delta H < 0$, $\text{hcp} \rightarrow \text{fcc} : \Delta H > 0$) and $\Delta T$ as the undercooling/overheating. The molar chemical Gibbs energy change $\Delta G_{m}^{\text{ch}}$ corresponds to the chemical driving force for the transformation and, as evident from Eq. (2), it changes its sign at $T_0$. The elastic strain energy per unit volume, $E_{\text{str}}^{\text{ch}}$, cannot be neglected since the product and the parent phases have unequal molar volumes (see section 5).

The volume of a product-phase particle is given by

$$V = \frac{n}{2} c \cdot r \cdot D \quad (3)$$

with $nc/2$ as the height/size of the nucleus; $n/2$ is the number of dislocations within the array of dislocations oriented perpendicular to the stacking direction (cf. FIG. 1 and FIG. 3; $n$ is the number of closed packed layers in the stack considered and $c$ is the distance between adjacent dislocations in the array parallel to the $c$-axis ($c_{\text{hcp}} = 0.40686 \text{ nm}$, $c_{\text{fcc}} = (2/3) \sqrt{3} a_{\text{fcc}} = 0.40931 \text{ nm}$ [34]), $2r$ is the separation distance of the partial dislocations ($r$ is the distance passed by one array of Shockley partial dislocations) and $D$ is the grain size of the parent crystal (cf. FIG. 1).
The newly created interfacial area $S$ of one particle is given by the top and the bottom side and the front and the rear side of the product-phase particle (as shown in FIG. 1). Because $D \geq nc/2$ the interfacial area $S$ is approximately given by the top and bottom sides and thus:

$$S \approx 2rD \quad (4)$$

It follows from Eqs. (1), (3) and (4):

$$\Delta G_A \equiv \frac{\Delta G}{rD} = n \frac{c}{2V_m} \left( \Delta G^{ch} + E_{str}^m \right) + 2\sigma \quad (5)$$

The term $\Delta G/rD$ corresponds to the energy difference between the product phase/particle and parent phase per unit area top/bottom interface, $\Delta G_A$. Note that both the volume chemical energy term as well as the interface energy term scale with $r$.

Evidently, a critical size (a critical value of $r$) does not occur (cf. Eq. (5)): The transformation can take place “spontaneously”, i.e. without overcoming an energy barrier by thermal activation, provided that the energy difference between the product phase (lying in-between the dissociated dislocation arrays) and parent phase per unit area, $\Delta G_A$, becomes negative, e.g. by a change of temperature (cf. Eqs. (2) and (5)). Hence, the product-phase particles develop by athermal nucleation.

The interfacial term $2\sigma$ in Eq. (5) is independent of the height $nc/2$ of the possibly operating dislocation array, whereas the chemical Gibbs energy change for operation of the same dislocation array $(=nc\Delta G^{ch}/2V_m)$ increases with $n$. For a fixed value of $n$ the energy difference per unit area top/bottom interface, $\Delta G_A$, equals zero at a finite value of undercooling, $\Delta T = T_0 - T$, for the $fcc\rightarrow hcp$ transformation (or rather overheating, $\Delta T = T_0 - T$, for the $hcp\rightarrow fcc$ transformation). A distribution of heights of the arrays of dislocations (corresponding with a varying number of closed packed layers, $n$, in the stack considered) is supposed to exist in the $fcc$ crystal. It follows from Eq. (5) that the larger the height of the dislocation array, i.e. the larger $n$, the lower the required
undercooling in order that this dislocation array starts to produce by glide a product-phase (hcp) particle. In other words, the nucleation event can be described as a kind of site saturation at each temperature, where dislocation arrays of specific height start to operate.

At a given undercooling, \( \Delta T(t) = T_0 - T(t) \), the critical (minimal) value of \( n \), i.e. \( n^* \), indicating the minimal height of the dislocation array for realising by glide the \( \text{fcc} \rightarrow \text{hcp} \) transformation, satisfies (see Eqs. (2) and (5)):

\[
n^*(\Delta T(t)) = \frac{2\sigma}{c} \left( \frac{\Delta H_{\text{hcp} \rightarrow \text{fcc}}}{2V_m T_0} (T_0 - T) + E_{\text{str}}^{*} \right)
\]

Depending on the values of the parameters at the right-hand side of Eq. (6), as \( \sigma, \Delta H \) and \( E_{\text{str}}^{*} \), a minimum number of stacked dislocations can be designated from \( n^* \) in order to obtain a stable nucleus that can grow. For example, considering the \( \text{hcp} \rightarrow \text{fcc} \) transformation above \( T_0 = 690 \text{ K} \), if \( \Delta H_{\text{hcp} \rightarrow \text{fcc}} = 501 \text{ J mol}^{-1} \), \( \sigma = 10 \text{ mJ m}^{-2} \) [8], \( E_{\text{str}}^{*} = 0.838 \text{ J m}^{-2} \), it follows \( n^* = 32 \) at \( T = 720 \text{ K} \) and \( n^* = 24 \) at \( T = 730 \text{ K} \). Upon decreasing temperature more and more dislocation arrays of decreasing height can become active. From experimental data for the martensitic transformation in Fe 30.2 wt% Ni, it was proposed that the cumulative number of operating dislocation arrays, \( N(n^*(\Delta T(t))) \), obeys the empirical function [35]:

\[
N(n^*(\Delta T(t))) = N_{\text{tot}} \exp(-n^*(\Delta T(t)))
\]

with \( N_{\text{tot}} \) as the total number of pre-existing Shockley partial dislocation arrays of variable height per unit volume. The total number of preexisting SP arrays of variable height can be (over)estimated by approximating the grain volume by \( D^3 \) and recognizing that \( D/c \) represents the number of dislocations covering a height \( D \). Hence, \( N_{\text{tot}} = 2 \cdot (D/c)/D^3 = 2/cD^2 \) taking into account that every perfect dislocation by dissociation contributes to the development of two nuclei (see FIG. 1). This estimation is rough as at the begin of the transformation the number of SPs in a nucleus is larger than one. However, the values of the fit parameters of the transformation model do
not depend strongly on the value of $N_{\text{tot}}$ (see section 5). The above treatment focussed on the $f_{\text{cc}} \rightarrow h_{\text{cp}}$ transformation occurring upon cooling. A parallel treatment holds for the $h_{\text{cp}} \rightarrow f_{\text{cc}}$ transformation occurring upon heating.

### 2.3 Interface-controlled growth

When an ordered array of Shockley partial dislocations glides through the crystal (as shown in FIG. 1 and FIG. 3) the product-phase particle grows. The dimensionality of the growth is one, i.e. the product-phase particle grows in one of the three possible $\langle 11\bar{3} \rangle$ directions oriented perpendicular to the $c$-axis (cf. FIG. 2). There is no composition change from parent to product phase in an allotropic phase transformation and thus the growth is controlled by atomic (jump) processes in the direct vicinity of the interface: interface-controlled growth.

The height of a product phase particle which starts to grow at time $\tau$ is given by

$$n^*(\Delta T(\tau))c/2 \quad (\text{cf. FIG. 1})$$. Hence, at time $t$ the volume $Y(\tau, t)$ of a product-phase particle, which starts to grow at time $\tau$, is given by (see FIG. 1, Eqs. (3) and (6))

$$Y(\tau, t) = D \frac{n^*(\Delta T(\tau))}{2} cr(T(t)) = D \frac{n^*(\Delta T(\tau))}{2} c \int_{\tau}^{t} v dt'$$

with $v$ as the interface/Shockley partial dislocation-glide velocity. For small undercooling or overheating the growth velocity $v$ is given by

$$v(T(t)) = M(\Delta G_m(T(t))) = M_0 \exp\left(\frac{-Q}{RT(t)}\right)(\Delta G_m(T(t)))$$

where $M$ is the temperature dependent interface mobility, $M_0$ is the pre-exponential factor for growth and $Q$ denotes the activation energy for growth. The net driving force $\Delta G_m(T(t))$ which is given as a molar quantity [21] amounts to (cf. Eqs. (1) and (5)):

$$\Delta G_m(T(t)) = \frac{\Delta G}{rDn^*(\Delta T(\tau))c/2V_m} = \Delta G_{m}^{\text{sh}}(T(t)) + E_{m}^{m}(T(t)) + \frac{2\sigma}{n^*(\Delta T(\tau))c/2V_m}$$
2.4 Extended Fraction, Transformed Fraction and Impingement

Adopting an appropriate impingement mode the real transformed fraction $f_{\text{model}}(T(t))$ can be calculated from the extended transformed fraction $x_e$ (cf. beginning of section 2). In the case of anisotropic growth, which pertains to the allotropic phase transformation considered here (one-dimensional growth; cf. section 2.3), the (hard) impingement process can be phenomenologically described by the following equation [21]:

$$\frac{df}{dx_e} = (1 - f)^\xi$$

(11)

where $\xi$ is a measure for the degree of anisotropic impingement. Integration of Eq. (11) for the case $\xi > 1$ yields:

$$f = 1 - \left[1 + (\xi - 1)x_e\right]^{-\frac{1}{\xi-1}}$$

(12)
3 Experimental

3.1 Alloy Production

The cobalt rod with a diameter of 5 mm used in this study was obtained in the hammered, not annealed state from Alfa Aesar (Karlsruhe, Germany) and has a purity of 99.995 at.%. Disc shaped specimens were produced by cutting pieces with a thickness of 750 µm. Both sides of the specimen discs were prepared by grinding with SiC-paper and subsequently polishing using diamond paste down to 0.25 µm such that all specimens have approximately the same mass of about 100 mg. All specimens were cleaned ultrasonically in isopropyl. After the calorimetric heat treatment the specimen discs were ground and polished again as mentioned above in order to reduce inhomogeneities of the surface as necessary for XRD and LM analysis.

3.2 Differential Scanning Calorimetry

The isochronal annealing was carried out with a power-compensated Differential Scanning Calorimeter (DSC) Pyris Diamond by Perkin Elmer. The temperature was calibrated using the melting temperature of zinc ($T_m = 692.15$ K [37]) measured for each heating rate used. Aluminum was used as pan material for both the specimen and reference container. Specimens of approximately the same mass were used in order to provide similar heat capacities. Pure argon gas with a constant flow was used as protective gas atmosphere. A measurement with empty pans served for determination of the baseline.

For each measurement in the temperature range from 523 K to 893 K at a heating rate varying from $10$ K min$^{-1}$ to $40$ K min$^{-1}$ a new specimen was used. In order to establish a microstructural reference state (see section 4), each specimen used for the kinetic analysis, was initially exposed to 60 isochronal transformation cycles with a cooling/heating rate of ±50 K min$^{-1}$ in a temperature range from 523 K to 893 K. The microstructure and phase composition of the specimens in the initial state and after the $1^{st}$, $2^{nd}$, $3^{rd}$, $10^{th}$, $20^{th}$, $40^{th}$ and $60^{th}$ isochronal transformation cycles were analyzed by LM and XRD.
For the calculation of the cumulative enthalpy $\Delta H(T(t))$, as function of temperature (time), the heat signal $d\Delta H(T(t))/dt$ was integrated for cumulative times. Previous to this integration, it is necessary to perform a baseline correction. This was done by subtracting the above mentioned DSC signal recorded with empty pans from the DSC signal recorded with the Co specimen for each heating rate [37]. This implies that the heat capacities of both phases are the same in the temperature region of the transformation, as holds for cobalt. The transformed fraction $f_{\text{exp}}(T(t))$ as function of temperature then is given by:

$$f_{\text{exp}}(T(t)) = \frac{\Delta H(T(t))}{\Delta H_{\text{hcp}\leftrightarrow fcc}}$$

(13)

where the total transformation enthalpy $\Delta H_{\text{hcp}\leftrightarrow fcc}$ was obtained by integration of the baseline corrected DSC signal over the entire temperature range of the transformation.

### 3.3 X-Ray Diffraction

XRD was employed for phase analysis and to characterize the crystalline imperfection upon thermal cycling. The X-ray diffraction measurements were performed with Mo Kα radiation employing a Bruker D8 Discover diffractometer operating in parallel-beam geometry equipped with an X-ray lens in the incident beam, a parallel-plate collimator in the diffracted beam and an energy-dispersive detector. The $2\theta$-range of 15° - 45° was measured with a step size of 0.015° and counting time per step of 10s.

### 3.4 Light Microscopy

The surface of the specimen discs before and after the 1st, 2nd, 3rd, 10th, 20th, 40th and 60th transformation cycles and of specimens used for the kinetic analysis were analysed using a Zeiss Axiophot light optical microscope. For that purpose the polished specimen discs were etched for 2 - 7 s using a fresh etching solution (14.3 vol.% H₂O, 14.3 vol.% CH₃COOH, 57.1 vol.% HCl and 14.3 vol.% HNO₃).
4 Results and Evaluation

A baseline-corrected isochronal DSC-Scan of Co at a heating rate of 20 K min\(^{-1}\) showing a heat signal associated with the \(hcpp\rightarrow fcc\) transformation is presented in FIG. 4. \(T_{\text{onset}}\) denotes the peak onset temperature, \(T_{\text{peak}}\) is the peak maximum temperature and \(\Delta H_{hcpp\rightarrow fcc}\) is the enthalpy of transformation (> 0 for the endothermic \(hcpp\rightarrow fcc\) transformation) given by the (hatched) area enclosed by the DSC signal and the baseline (\textit{dashed}).

(insert here Figure 4)

In order to characterize the \(hcpp\rightarrow fcc\) transformation behaviour and the microstructural evolution upon thermal cycling of initially heavily deformed Co, the change of the DSC heat signal (characterized by the parameters indicated above), XRD diffractograms and the change of the grain size were recorded as a function of the number of transformation cycles experienced (one cycle is \(hcpp\rightarrow fcc\) followed by \(fcc\rightarrow hcpp\)). Results are presented in FIG. 5.

The variation of the parameters \(T_{\text{onset}}, T_{\text{peak}}\) and \(\Delta H_{hcpp\rightarrow fcc}\) for the \(hcpp\rightarrow fcc\) transformation (see FIG. 4) is shown in FIG. 5a as a function of the number of transformation cycles at a heating rate of 50 K min\(^{-1}\) between 523 K and 893 K. Starting from the heavily deformed initial state, the parameters \(T_{\text{onset}}, T_{\text{peak}}\) and \(\Delta H_{hcpp\rightarrow fcc}\) decrease from the 1\(^{\text{st}}\) to the 2\(^{\text{nd}}\) transformation cycle from 736.3 K, 746.9 K and 406 J mol\(^{-1}\) to 717.1 K, 735.6 K and 385 J mol\(^{-1}\), followed by an increase between the 2\(^{\text{nd}}\) and 3\(^{\text{rd}}\) transformation cycle to 721.9 K, 738.7 K and 452 J mol\(^{-1}\), respectively. After the 3\(^{\text{rd}}\) transformation cycle \(T_{\text{onset}}\) and \(T_{\text{peak}}\) pass through modest local maxima of about 722.3 K and 739.0 K, respectively. Eventually \(T_{\text{peak}}\) and \(T_{\text{onset}}\) approach asymptotically equilibrium values of about 735.7±0.2 K (average of the last 40 transformation cycles) and about 726.5±0.2 K (average of the last 20 transformation cycle), respectively.
The total transformation enthalpy, $\Delta H_{hcp\rightarrow fcc}$, shows a steep increase from the 2\textsuperscript{nd} to the 4\textsuperscript{th} transformation cycle and approaches an equilibrium value after about 20 transformation cycles of about 500±3 J mol\(^{-1}\) (average of the last 40 transformation cycles). The small values of $\Delta H_{hcp\rightarrow fcc}$ observed in the first cycles suggest that the specimen only experiences a fractional $hcp\rightarrow fcc$ transformation during the first cycles.

XRD measurements of Co specimens at room temperature in the initial state and after the 1\textsuperscript{st}, 2\textsuperscript{nd} and 3\textsuperscript{rd} transformation cycles (inset in FIG. 5b) reveal 111 and 002 reflexes of the fcc Co phase after (only) the 1\textsuperscript{st} and 2\textsuperscript{nd} transformation cycle (Cards 89 4308 for hcp-Co and 15 0806 for fcc-Co of the powder diffraction file [38], were used for phase identification). In the initial state, after the 3\textsuperscript{rd} transformation cycle and during further cycling no fcc Bragg peaks could be detected. These XRD results support the above interpretation of the $\Delta H_{hcp\rightarrow fcc}$ changes during cycling.

Hence, the amount of hcp and fcc Co at room temperature after a specific number of transformation cycles can be deduced from the enthalpy data adopting direct proportionality of $\Delta H_{hcp\rightarrow fcc}$ with the amount of hcp present before the hcp$\rightarrow$fcc transformation takes place. The thus determined fractional amounts of hcp and fcc phase at room temperature are shown in FIG. 5b as function of the number of transformation cycles. The amount of fcc Co at room temperature reaches a maximum of about 25 % after two transformation cycles followed by a decrease towards nil reached at about the 5\textsuperscript{th} transformation cycle.

The full width at half maximum (FWHM) was calculated for the 100, 002, 101, 102 110 and 103 reflexes of hcp Co. The FWHM results as obtained for the initial state and after the 1\textsuperscript{st}, 2\textsuperscript{nd}, 3\textsuperscript{rd}, 10\textsuperscript{th}, 20\textsuperscript{th}, 40\textsuperscript{th} and 60\textsuperscript{th} transformation cycles are presented in FIG. 5c as function of the corresponding transformation cycle number. For all reflexes a steep decrease can be observed from the values corresponding to the initial state to the values obtained after the 2\textsuperscript{nd}/3\textsuperscript{rd} transformation cycle. This decrease can be ascribed to a reduction of lattice defects in the initially heavily
deformed state upon annealing (recovery), grain growth and transformation cycling. For all reflexes the FWHM and thus the defect structure remains about constant after the 3rd transformation cycle.

The change of the mean grain size, $D$, as determined by LM, is shown in FIG. 5d as function of the number of transformation cycles. It was not possible to measure the grain size of Co in the initial stage because the etched microstructure did not allow a clear identification of grain boundaries: the highly deformed initial state leads to an uncontrollable etching process. The grain size increases upon thermal cycling from initially less than 10 µm to about 87±5 µm after the 40th cycle and remains constant thereafter.

(insert here Figure 5)

It has been concluded from the above results that, to assure the same initial state for each experiment used for kinetic analysis, each such specimen will be subjected to 60 transformation cycles before a kinetic analysis is performed.

Important morphological characteristics are revealed by LM from the specimen surfaces, as shown for the 10th, 40th and 60th transformation cycles in FIGs. 6a-c. After the 10th cycle (FIG. 6a) the etching suggests an underlying transformation structure exhibiting different, specific orientations of martensite plates within a Co grain. After the 40th cycle (FIG. 6b) the etching suggests that only a single specific orientation is associated with the martensitic transformation experienced by a grain. After the 60th transformation cycle no such etch effect is observed (cf. FIG. 10 and its discussion in section 6.1).

(insert here Figure 6)
5 Analysis of the Transformation Kinetics

Baseline corrected isochronal DSC scans for the allotropic $hcp\rightarrow fcc$ (upon heating) and $fcc\rightarrow hcp$ (upon cooling) transformations in Co measured at heating/cooling rates in the range from $10\ K\ min^{-1}$ to $40\ K\ min^{-1}$ are presented in FIG. 7. The enthalpy of transformation for the $hcp\rightarrow fcc$ transformation (upon heating; independent of heating rate) is about $+501\pm 7\ J\ mol^{-1}$ and for the $fcc\rightarrow hcp$ transformation (upon cooling; independent of cooling rate) about $-512\pm 13\ J\ mol^{-1}$, i.e. within the experimental accuracy the $hcp\rightarrow fcc$ and $fcc\rightarrow hcp$ transformations exhibit the same absolute value for the enthalpy of transformation.

(insert here Figure 7)

The cooling curves in FIG. 7, i.e. for the $fcc\rightarrow hcp$ transformation, have been included for the sake of completeness. Whereas the start temperature for the $fcc\rightarrow hcp$ transformation (upon cooling) clearly depends on the cooling rate applied, this is much less the case (if at all) for the dependence of the start temperature of the $hcp\rightarrow fcc$ transformation (upon heating) on heating rate (see FIG. 7). In both cases, i.e. for the transformation upon cooling and the transformation upon heating, a cooling/heating rate independent start temperature is expected in view of the athermal value of the nucleation process (see section 2.2). It must be noted, that no temperature calibration of the DSC for the cooling part of the cycle is possible and that the DSC signal during cooling is smeared distinctly, as is well known for power-compensated DSCs [37]. Therefore, the cooling-rate dependence of the start temperature of the transformation upon cooling has to be considered as an artifact from the measurement and the cooling curves cannot be used for kinetic analysis.

The kinetic analysis of the allotropic $hcp\rightarrow fcc$ transformation of Co was performed applying the modular phase transformation model in the form as described in section 2.
The experimental transformation rates \( \frac{df_{\text{exp}}}{dT} \) ( \( \frac{df_{\text{exp}}}{dT} = \frac{1}{\Phi} \frac{df_{\text{exp}}}{dt} \) ) have been plotted in FIG. 8 as function of the transformed fraction \( f_{\text{exp}}(T(t)) \) for the different heating rates. The corresponding curves for the experimentally determined transformed fractions \( f_{\text{exp}}(T(t)) \) (see section 3.2, equation (13)) are shown in FIG. 9 as function of temperature \( T(t) \). Evidently, the maximum transformation rate occurs at \( f_{\text{exp}} < 1 - 1/e \). This is a strong indication for anisotropic growth [39] as expected for the \( \text{hcp} \rightarrow \text{fcc} \) transformation in Co (cf. sections 2.2 and 2.3). The impingement mode for anisotropic growth (introduced in section 2.4) has thus been used in the kinetic model of the phase transformation.

(insert here Figure 8)

The kinetic model parameters \( \sigma, Q \) and \( \xi \) were determined by numerically fitting of the model to simultaneously all isochronal heating runs obtained for various heating rates in the range from 10 K min\(^{-1}\) to 40 K min\(^{-1}\). The mean square error (MSE) between the calculated (calc) and experimental (exp) transformed fraction curves was minimized by varying the fit parameters using a multidimensional unconstrained nonlinear minimization fitting routine [40] as implemented in MATLAB for each \( i \)th of the applied heating rates

\[
MSE = \sum_{i=1}^{N} \left( \frac{\text{exp} - \text{calc}}{\text{exp}} \right)^2
\]  

(14)

The results of the fitting as described above are shown in FIG. 9 (experimental data: symbols; fit: lines) and Table 1 (i.e. the values thus determined for \( \sigma, Q \) and \( \xi \)).

(insert here Figure 9)
Values used for the constants in the model have (also) been given in Table 1. The total number of pre-existing dislocations \( N_{\text{tot}} \) within a grain of mean size \( D = 87\pm5 \, \mu\text{m} \) was calculated as described in section 2.2 as \( 6.5\times10^{17} \, \text{m}^{-3} \). The total enthalpy of transformation was taken as \( \Delta H_{\text{hcp-fcc}} = 501\pm7 \, \text{J mol}^{-1} \), as determined experimentally (cf. section 4). The strain energy contribution expressed as \( E_{\text{str}} \), corresponding with the macroscopic distortion discussed in sections 2.1 and 2.2, was estimated according to [19] at about \( 0.838 \, \text{J mol}^{-1} \) under the assumption of linear elasticity and coherency (full elastic accommodation of volume misfit).

It is supposed that dislocation glide is rate controlled by thermal activation as it generally holds for materials with metallic bonding type. In pure metals it is assumed that the atomic structure within the closest packed glide plane represents a weak lattice resistance. The mobility of these dislocations is thus determined by thermal fluctuations characterized by an activation energy \( Q \) [41].

The temperature-independent dislocation/interface velocity \( \nu_0 \) was estimated by using the well-known (empirical) expression for the pre-exponential factor for lattice-resistance controlled glide of dislocations in metals (i.e. rate limited by weak discrete obstacles) (as validated for a wide range of metals [42]), which reads \( \dot{\gamma}_0 = \nu_0 \rho_m b = 10^9 \, \text{s}^{-1} \) with \( \rho_m \) as the dislocation density and \( b \) as the Burgers vector taken equal to \( 1/2\sqrt{2}a_{\text{fcc}} \) with \( a_{\text{fcc}} = 0.35447 \, \text{nm} \) [34]. The density of mobile dislocations can be estimated according to [42] as \( 10^{13} \, \text{m}^{-2} \) lying in the range of values expected for fcc and hcp metals. The thus obtained value for \( \nu_0 \) is about \( 400 \, \text{m s}^{-1} \). Thus the mobility \( M_0 = \nu_0/RT \) [21] was assessed at \( 4.3 \, \text{m} \cdot \text{mol} \cdot \text{J}^{-1} \cdot \text{min}^{-1} \), adopting a mean value for the temperature \( T = 700 \, \text{K} \). Note that the temperature dependence of \( M_0 \) is small in comparison to the temperature dependence of the exponential term in \( M \) (see Eq. (9)) and thus the temperature dependence of \( M_0 \) can be neglected.
The influence of a variation of the constant parameters $N_{\text{tot}}$, $T_0$ and $M_0$ on the fit parameters, as indicated by $N_{\text{tot}} = 6.5 \cdot 10^{17} \pm 1 \text{ m}^{-3}$, $T_0 = 690 \pm 1 \text{ K}$ and $M_0 = 4.3 \cdot 10^{0} \pm 1$, yielded variations of $\sigma$ and $Q$ as indicated in Table 1; the impingement parameter $\xi$ is not influenced.

6 Discussion

6.1 Preceding transformation cycles

Each Co specimen used for kinetic analysis was subjected to a number of 60 preceding transformation cycles to assure similar starting conditions (same microstructure) and full transformation (see section 4). The phenomenon can be interpreted as that the preceding transformation cycles are needed to stabilize the dislocation configuration (cf. section 2.1) in the specimen that carries the forward ($\text{hcp} \to \text{fcc}$) and backward ($\text{fcc} \to \text{hcp}$) transformations.

The initially incomplete transformation can partly be ascribed to the relatively strong interaction of the (partial) dislocations with the grain boundaries: upon increasing grain size during cycling (see FIG. 5d) relatively more dislocations become available for establishing the transformation [1, 2, 10].

During the first transformation cycles the transformations occur in conjunction with recovery, possible (local) recrystallisation and grain growth in order to reduce the stored plastic deformation and grain-boundary surface. This leads to changes of the (initially disarranged) dislocation structure. A further complication is that after a first $\text{hcp} \to \text{fcc}$ transformation upon heating, that then, upon subsequent cooling, a completely reverse formation of $\text{hcp}$ Co requires glide of SPs on the closest packed $\{111\}_{\text{fcc}}$ planes lying parallel to the previous $\{0001\}_{\text{hcp}}$ planes. However, at least initially SPs may be available as well on $\{111\}_{\text{fcc}}$ planes not parallel to the former $\{0001\}_{\text{hcp}}$ plane and thus the original $\text{hcp}$ grain microstructure is not re-established (Note the variously orientated $\text{hcp}$ Co martensite “plates” in a single grain in FIG. 6a). As a consequence, this reasoning provides a further reason (see above) why the transformation cannot run to completion in such a grain; a small amount of parent phase is retained (see FIG. 5b and its inset).
The above described transformation behaviour for the first transformation cycles is compatible with the DSC results. The decrease of \( T_{\text{onset}} \) and \( T_{\text{peak}} \) found for the 2nd transformation cycle can be understood such that during the first complete hcp \( \rightarrow \) fcc cycle the disordered dislocation structure of the initial state evolves into a more ordered (in the sense of the discussion in section 2.1) dislocation structure, thereby facilitating the transformation: less overheating is required (see section 2.2).

6.2 Kinetics

The evaluation of the kinetics of the allotropic hcp \( \rightarrow \) fcc phase transformation in Co performed in section 0 demonstrates that this transformation can be well described as governed by the activation of pre-existing nuclei (stacked dislocation sequences) and thermally activated interface-controlled growth subjected to anisotropic impingement. The resulting values for the fit parameters \( \sigma \), \( Q \) and \( \xi \) agree well with data provided by theory and experiment (see what follows).

The investigation of dislocation nodes (the extension of a dislocation node depends amongst others on the stacking fault energy produced by the node) in pure Co [8] and Fe-Cr-Ni alloys [43] yielded stacking fault energy values from 5 to 10 mJ m\(^{-2}\). This agrees very well with the here determined value for the interface (= stacking fault) energy resulting from model fitting of the transformation kinetics yielding \( \sigma = 6.7 \pm 0.4 \) mJ m\(^{-2}\).

The above discussion leads to a summarizing schematic presentation of the evolving dislocation structure in a grain during hcp \( \rightarrow \) fcc (thermal) cycling as presented in FIG. 10.

(Prolonged thermal cycling leads to an increase of the thickness of the martensite "plates" (FIG. 6b) i.e. the height of the operating dislocation array increases, and a single glide variant appears to become dominant (cf. FIG. 6b and c) [6, 10].)
The ratio of the activation energy for diffusion and the activation energy for dislocation glide controlled by lattice resistance is for metals about 7 [42]. The activation energy for self diffusion of Co is $Q_{\text{Co}} = 270 \text{ kJ mol}^{-1}$ [2]. Indeed, $1/7 \cdot Q_{\text{Co}} \approx 38 \text{ kJ mol}^{-1}$ which is well compatible with the here determined value of the activation energy for growth, $Q = 33 \pm 15 \text{ kJ mol}^{-1}$, thereby validating the applied concept of growth controlled by dislocation glide.

7 Conclusions

- Extensive thermal cycling of Co in a fixed temperature range is necessary to establish full reversibility of the allotropic $\text{hcp} \leftrightarrow \text{fcc}$ phase transformation (i.e. reaching constant values of $T_{\text{onset}}$, $T_{\text{peak}}$ and $\Delta H_{\text{hcp} \rightarrow \text{fcc}}$). During thermal cycling stabilization of the dislocation structure is established such that in a single grain the $\text{hcp} \leftrightarrow \text{fcc}$ transformation is established by (ideally) only one single stack of ordered perfect dislocations (in $\text{fcc}$) = 2 parallel stacks of ordered Shockley partial dislocations (in $\text{hcp}$), implying that only one (of the maximally four) glide-plane types operates within a single grain.

- The kinetics of the transformation can be well described on the basis of a modular transformation model adopting an athermal nucleation mode and an anisotropic interface-controlled growth mode.

- Results obtained for the fit parameters $\sigma (= 6.7 \pm 0.4 \text{ mJ m}^{-2})$ and $Q (= 33 \pm 15 \text{ kJ mol}^{-1}$) are well compatible with the interpretation of the product/parent interface as a stacking fault and of the growth process as realized by thermally activated glide of Shockley partial dislocations.
References

[1] F. Sebilleau, and H. Bibring (ed), *The Mechanism of Phase Transformation in Metals*, London, Institute of Metals. 18 (1955) 209

[2] Cobalt Monograph, Centre d’Information du Cobalt. Brussels (1960)

[3] O. S. Edwards, and H. Lipson, J. Inst. Metal. 69 (1943) p. 177

[4] J. B. Hess, and C. S. Barrett, J. Met. 4 (1952) 645

[5] E. A. Owen, and D. Madoc Jones, Proc. Phys. Soc. London Sec. B 67 (1954) p. 456

[6] E. Votava, J. Inst. Metal. 90 (1961) p. 129

[7] J. O. Nelson, and C. J. Altstetter, Trans. Metall. Soc AIME 230 (1964) p. 1577

[8] T. Ericsson, Acta Metall. 14 (1966) p. 853

[9] R. Hultgren, P. D. Desai, and D. T. Hawkins, *Selected Values of the Thermodynamic Properties of the Elements*. American Society of Metals, Ohio (1973)

[10] A. Munier, J. E. Bidaux, R. Schaller, and C. Esnouf, J. Mat. Res. 5 (1990) p. 769

[11] H. T. Hesemann, P. Müllner, and E. Arzt, Scr. Mater 44 (2000) p. 795

[12] M. Lin, G. B. Olson, and M. Cohen, Metall. Trans. 7A (1976) p. 1897.

[13] J. T. Hesseman, P. Müllner, C. Kraft, and E. Arzt, J. Phys. IV 112 (2003) p. 107

[14] A. T. W. Kempen, F. Sommer, and E. J. Mittemeijer, Acta Mater. 50 (2002) p. 1041.

[15] H. Nitsche, F. Sommer, and E. J. Mittemeijer: Metall. Mater. Trans. A 37A (2006) p. 621.

[16] H. Nitsche, M. Stanislawski, F. Sommer, and E. J. Mittemeijer: Z. Metallkd. 96 (2005) p. 1341.

[17] H. Nitsche, F. Sommer, and E. J. Mittemeijer: J. Non-Cryst. Solids 351 (2005) p. 3760.

[18] F. Liu, Sommer, and E. J. Mittemeijer: Acta. Mater. 52 (2004) p. 3207.

[19] A. T. W. Kempen, F. Sommer, and E. J. Mittemeijer: Acta. Mater. 50 (2002) p. 3545.

[20] Y. C. Liu, F. Sommer, and E. J. Mittemeijer: Acta. Mater. 51 (2003) p. 507.

[21] A. H. Cottrell, *The Mechanical Properties of Matter*, John Wiley & Sons, New York (1964)

[22] P. Villars, and L. D. Calvert, *Pearson's Handbook of Crystallographic Data for Intermetallic Phases I*, ASM International, Materials Park, Ohio, (1997).

[23] E.-S. Lee, and Y. G. Kimm, Acta Metall. Mater. 38 (1990) p. 1677.

[24] G. W. H. Höhne, W. F. Hemminger, and H.-J. Flammersheim, *Differential Scanning Calorimetry*, Berlin Heidelberg : Springer-Verlag, (2003)

[25] International Centre of Diffraction Data. Newton Square, PA, USA (1997-2007)

[26] F. Liu, S. J. Song, F. Sommer, and E. J. Mittemeijer, Acta. Metall. Mater. 57 (2009) p. 6176.

[27] J. A. Nelder, and R. Mead, Comput. J. 7 (1965) p. 308.
[41] J. E. Dorn, *Mechanical Behavior of Materials at elevated Temperatures*, McGraw-Hill Book Company, Inc., New York (1961)

[42] J. F. Frost, and M. F. Ashby, *Deformation-Mechanism Maps*, Oxford: Pergamon Press (1982)

[43] F. Lecroisey, and A. Pineau, Metall. Trans. 3 (1972) p. 387
Tables with captions

Table 1. Overview of the constants used in the adopted modular phase transformation model (see section 2), as well as the values obtained for the fit parameters by fitting this model to, simultaneously, all isochronal DSC scans upon heating.

| parameter                        | value            | source                                  |
|----------------------------------|------------------|-----------------------------------------|
| **constants**                    |                  |                                         |
| enthalpy, $\Delta H_{hcp\rightarrow fcc}$ | 501±7 J·mol⁻¹    | experiment; this work                   |
| grain size, $D$                  | 87 $\mu$m        | experiment; this work                   |
| lattice parameter, $c$           | 0.40686 nm       | [34]                                    |
| equilibrium temperature, $T_0$   | 690±7 K          | [4]                                     |
| total number of pre-existing dislocations, $N_\text{tot}$ | $6.5\cdot10^{17}$ m⁻³ | $N_\text{tot} = 2/\pi D^2$; this work |
| strain energy, $E_{\text{Str}}$  | 0.838 J·mol⁻¹    | according to [19]                       |
| mobility, $M_0$                  | 4.3 m·mol⁻¹J⁻¹min⁻¹ | $M_0 = v_0/RT$; this work               |
| interface energy, $\sigma$      | 6.8±0.4 mJ·m²    |                                         |
| activation energy for growth, $Q$| 33±15 kJ·mol⁻¹   |                                         |
| impingement parameter, $\xi$    | 1.35             | -                                       |
Figure captions

Figure 1. Schematic view of an hcp nucleus (ABABAB… stacking sequence) developing in an fcc matrix (ABCABC… stacking sequence) by dissociation of three perfect dislocations in fcc. Left: Array of three perfect dislocations in the fcc Co phase (before dissociation); right: two arrays each consisting of three Shockley partial dislocations; the two arrays build up two particles consisting of the hcp phase, each particle having a volume determined by the grain size $D$, the height of the defect structure (depending on the number of Shockley partial dislocations within the array) and half of the separation distance, $2r$, realised by glide of the Shockley partial dislocations.

Figure 2. Stacking sequence of an fcc crystal lattice (top). The black arrows indicate possible Burgers vectors available for the glide process of Shockley partial dislocations upon the $fcc\rightarrow hcp$ transformation. Bottom left: Burgers vectors of Shockley partial dislocations in every second closest packed plane oriented such that for three successive Shockley partials (i.e. comprising a stack of six closest packed planes) $\vec{b}_1 + \vec{b}_2 + \vec{b}_3 = 0$. No macroscopic shear occurs. Bottom right: Shockley partial dislocations, gliding on every second closest packed plane with the same Burgers vector. This leads to macroscopic shear.

Figure 3. Ordered arrays of Shockley partial dislocations gliding through an fcc Co crystal leaving behind the hcp Co structure (see also FIG. 1).

Figure 4. Heat signal corresponding to the endothermic hcp$\rightarrow$fcc transformation in Co (after 61$^{st}$ cycles) obtained upon isochronal heating at a rate of 20 K min$^{-1}$

Figure 5. Results of DSC, XRD and LM analysis as function of the number of transformation cycles. (a) $T_{onset}$, $T_{peak}$ and $\Delta H_{hcp\rightarrow fcc}$ at a heating rate of 50 K min$^{-1}$, (b) phase fraction as deduced
from the enthalpy data in (a) (see text); *inset*: 111 and 002 reflexes of *fcc* phase and 002 reflexes of *hcp* phase before and after the 1st, 2nd and 3rd cycles, (c) FWHM of selected XRD reflexes as indicated and (d) grain size.

Figure 6. Light optical micrographs of the etched microstructure of the surface of Co specimens after the (a) 10th, (b) 40th and (c) 60th transformation cycle performed in the DSC at a rate of \( \pm 50 \text{ K min}^{-1} \) in the temperature range from 523 K to 893 K. The etched microstructure suggests (see the arrows) that upon prolonged annealing the number of types of glide planes operating during the martensitic transformation (the *fcc* \( \rightarrow \) *hcp* experienced in the cooling part of the transformation cycle) in a single grain is reduced to one (see text and section 6.1).

Figure 7. Isochronal baseline corrected DSC-scans for Co (after 60 transformation cycles) at various heating rates as indicated.

Figure 8. The experimental transformation rate \( \frac{df_{\text{exp}}}{dT} \) as function of the transformed fraction for the *hcp* \( \rightarrow \) *fcc* transformation for various heating rates. The plots show maxima at positions left with respect to the position \( f = 1 - \frac{1}{e} \), indicating an anisotropic impingement mode [39].

Figure 9. Isochronal DSC curves (symbols) and model fit (simultaneously to all runs) using the modular phase transformation model (\( \sigma, Q \) and \( \xi \) as fit parameters) for the allotropic phase transformation *hcp* \( \rightarrow \) *fcc* of Co.

Figure 10. Schematic presentation of the dislocation structure development in Co upon *hcp* \( \leftrightarrow \) *fcc* (thermal) cycling.

(a) The initial state represents (severely deformed) *hcp* Co as formed by dissociation of arrays of perfect dislocations and subsequent “ordered” glide of SPs on every second closest packed {111}
plane in the parent \( fcc \) Co. The whole grain could not transform to \( hcp \) Co because of blocking of
the growing martensite “plates” growing by “ordered” glide of arrays of SPs; each stack of SPs
slides along one of the four equivalent types of \( \{111\}_{fcc} \) planes.

(b) + (c) Upon continued thermal cycling the height of the (remaining, active) stacks of arrays of
(partial) dislocations (perpendicular to \( \{0001\}_{hcp}/\{111\}_{fcc} \) planes) increases, due to pick up of
neighbouring dislocations, pushing aside unfavourably oriented smaller dislocation stacks, e. g. by
limiting the associated SP glide, and by even driving them back (in associated form) into the grain
boundaries (as illustrated in the figure; cf. (a) and (c)).

(d) + (e) Eventually, upon prolonged thermal cycling, a dislocation structure emerges that realizes
the \( hcp \leftrightarrow fcc \) transformation on the basis of (ideally) one single stack of ordered perfect dislocations
(in \( fcc \)) = 2 parallel stacks of ordered Shockley partial dislocations (in \( hcp \)) implying that only one
(instead of, maximally, four; see (a) + (b)) glide plane system operates within a single grain, e. g.
\[
(111)_{fcc} \parallel (0001)_{hcp}, \quad [\bar{T}10]_{fcc} \parallel [T0\bar{T}0]_{hcp}.
\]
Schematic view of an hcp nucleus (ABABAB... stacking sequence) developing in an fcc matrix (ABCABC... stacking sequence) by dissociation of three perfect dislocations in fcc. Left: Array of three perfect dislocations in the fcc Co phase (before dissociation); right: two arrays each consisting of three Shockley partial dislocations; the two arrays build up two particles consisting of the hcp phase, each particle having a volume determined by the grain size D, the height of the defect structure (depending on the number of Shockley partial dislocations within the array) and half of the separation distance, 2r, realised by glide of the Shockley partial dislocations.

63x43mm (600 x 600 DPI)
Stacking sequence of an fcc crystal lattice (top). The black arrows indicate possible Burgers vectors available for the glide process of Shockley partial dislocations upon the fcc→hcp transformation.

Bottom left: Burgers vectors of Shockley partial dislocations in every second closest packed plane oriented such that for three successive Shockley partials (i.e. comprising a stack of six closest packed planes). No macroscopic shear occurs. Bottom right: Shockley partial dislocations, gliding on every second closest packed plane with the same Burgers vector. This leads to macroscopic shear.

57x42mm (600 x 600 DPI)
Ordered arrays of Shockley partial dislocations gliding through an fcc Co crystal leaving behind the hcp Co structure (see also FIG. 1).
Heat signal corresponding to the endothermic hcp→fcc transformation in Co (after 61st cycles) obtained upon isochronal heating at a rate of 20 K min⁻¹.
Results of DSC, XRD and LM analysis as function of the number of transformation cycles. (a) Tonset, Tpeak and Delta H
hcp→fcc at a heating rate of 50 K min⁻¹, (b) phase fraction as deduced from the enthalpy data in (a) (see text); inset: 111 and 002 reflexes of fcc phase and 002 reflexes of hcp phase before and after the 1st, 2nd and 3rd cycles, (c) FWHM of selected XRD reflexes as indicated and (d) grain size.
Light optical micrographs of the etched microstructure of the surface of Co specimens after the (a) 10th, (b) 40th and (c) 60th transformation cycle performed in the DSC at a rate of ±50 K min⁻¹ in the temperature range from 523 K to 893 K. The etched microstructure suggests (see the arrows) that upon prolonged annealing the number of types of glide planes operating during the martensitic transformation (the fcc→hcp experienced in the cooling part of the transformation cycle) in a single grain is reduced to one (see text and section 6.1).
Isochronal baseline corrected DSC scans for Co (after 60 transformation cycles) at various heating rates as indicated.

\[ H_{\text{hcp} \rightarrow \text{fcc}} \approx +501 \pm 7 \text{ J/mol} \]
\[ H_{\text{hcp} \leftarrow \text{fcc}} \approx -512 \pm 13 \text{ J/mol} \]
The experimental transformation rate \( \frac{df_{\text{exp}}}{dT} \) as function of the transformed fraction for the hcp→fcc transformation for various heating rates. The plots show maxima at positions left with respect to the position \( f = 1 \ 1/e \), indicating an anisotropic impingement mode [39].

109x79mm (600 x 600 DPI)
Isochronal DSC curves (symbols) and model fit (simultaneously to all runs) using the modular phase transformation model (□, Q and □ as fit parameters) for the allotropic phase transformation hcp→fcc of Co.

http://mc.manuscriptcentral.com/pm-pml
Schematic presentation of the dislocation structure development in Co upon hcp□fcc (thermal) cycling.
(a) The initial state represents (severely deformed) hcp Co as formed by dissociation of arrays of perfect dislocations and subsequent “ordered” glide of SPs on every second closest packed {111} plane in the parent fcc Co. The whole grain could not transform to hcp Co because of blocking of the growing martensite “plates” growing by “ordered” glide of arrays of SPs; each stack of SPs glides along one of the four equivalent types of {111}fcc planes.
(b) + (c) Upon continued thermal cycling the height of the (remaining, active) stacks of arrays of (partial) dislocations (perpendicular to {0001}hcp/{111}fcc planes) increases, due to pick up of neighbouring dislocations, pushing aside unfavourably oriented smaller dislocation stacks, e. g. by limiting the associated SP glide, and by even driving them back (in associated form) into the grain boundaries (as illustrated in the figure; cf. (a) and (c)).
(d) + (e) Eventually, upon prolonged thermal cycling, a dislocation structure emerges that realizes the hcp□fcc transformation on the basis of (ideally) one single stack of ordered perfect dislocations (in fcc) = 2 parallel stacks of ordered Shockley partial dislocations (in hcp) implying that only one (instead of, maximally, four; see (a) + (b)) glide plane system operates within a single grain, e. g. .