Article

Measurement and Evaluation of Calorimetric Descriptors for the Suitability for Evolutionary High-Throughput Material Development

Anastasiya Toenjes ^{1,*}, Heike Sonnenberg ¹, Christina Plump ², Rolf Drechsler ² and Axel von Hehl ¹

¹ Leibniz Institute for Materials Engineering IWT, University of Bremen, Badgasteiner Str. 3, 28359 Bremen, Germany; sonnenberg@iwt-bremen.de (H.S.); vonhehl@iwt-bremen.de (A.v.H.)

² Department of mathematics and computer science, University of Bremen, Bibliothekstraße 5, 28359 Bremen, Germany; cplump@uni-bremen.de (C.P.); drechsler@uni-bremen.de (R.D.)

* Correspondence: toenjes@iwt-bremen.de; Tel.: +49-421-218-51491

Received: 3 December 2018; Accepted: 25 January 2019; Published: 29 January 2019

Abstract: A novel method for evolutionary material development by using high-throughput processing is established. For the purpose of this high-throughput approach, spherical micro samples are used, which have to be characterized, up-scaled to macro level and valued. For the evaluation of the microstructural state of the micro samples and the associated micro-properties, fast characterization methods based on physical testing methods such as calorimetry and universal microhardness measurements are developed. Those measurements result in so-called descriptors. The increase in throughput during calorimetric characterization using differential scanning calorimetry is achieved by accelerating the heating rate. Consequently, descriptors are basically measured in a non-equilibrium state. The maximum heating rate is limited by the possibility to infer the microstructural state from the calorimetric results. The substantial quality of the measured descriptors for micro samples has to be quantified and analyzed depending on the heating rate. In this work, the first results of the measurements of calorimetric descriptors with increased heating rates for 100Cr6 will be presented and discussed. The results of low and high heating rates will be compared and analyzed using additional microhardness measurements. Furthermore, the validation of the method regarding the suitability for the evolutionary material development includes up-scaling to macro level and therefore different sample masses will be investigated using micro and macro samples during calorimetry.

Keywords: material development; characterization methods; high-throughput; calorimetry; descriptors

1. Introduction

At the Collaborative Research Center ‘Farbige Zustände’ (CRC 1232) of the German Research Foundation (DFG), a novel method for evolutionary structural material development has been established. A sequence of different characterization processes has been developed using spherical micro samples with a diameter equal to or less than 1 mm, thus enabling high-throughput screening. Droplet generators as in [1] provide spherical droplets as micro samples, allowing fast production of various alloys while using small batches. Starting with chemical composition, the experimental processes of the different characterization methods are systematically adapted, including the variation of the thermal, thermo-mechanical and mechanical parameters involved. Subsequently, the obtained microstructure states and associated micro-properties are characterized, up-scaled to macro level and valued. By means of machine learning and heuristic methods, the experimental plans are refined and

the experimental procedure is continued until, finally, a novel material with the desired properties is found [2,3].

The properties of metallic materials are substantially affected by the phases present in the microstructure and their special morphology. Furthermore, the interactions of defects of the respective phases play a decisive role for many metallurgical processes. Defect structure and microstructure are significantly influenced by the heat treatment and the transformation processes taking place, such as the dissolution and precipitation of phases or the change of the crystal structure, but also by the alloy.

Most metallic materials strive to form an equilibrium phase which is counteracted by rapid heating and cooling processes. Due to the important thermal switching behavior and the small Biot number, small-scale samples enable rapid temperature changes in the material and thus the possibility of non-equilibrium states.

Dynamic differential scanning calorimeters (DSC) are used for heat treatment and in situ characterization of structural changes, as well as for rapid ex situ characterization of previously heat-treated samples. The chemical and physical reactions of steel and aluminum materials due to heating or cooling processes during DSC measurements can be investigated. Using this measuring technique, extremely variable temperature–time cycles can be adjusted so that they are device-specifically limited for the maximum temperature, as well as with respect to heating and cooling rates. Not only phase transition, but also precipitation and dissolution processes are detectable during DSC measurements, which can be used as a characterization of microstructural states. Several studies regarding DSC measurements on steels can be found in the literature, e.g., concerning the determination of martensite decay [4]. In the case of aluminum alloys, extensive work has already been carried out on precipitation and dissolution behavior using DSC from Keßler et al. [3], in which methods for producing continuous cooling precipitation diagrams, as well as continuous heating dissolution diagrams, were developed. Measuring speed, and thus sample throughput, can be increased using non-equilibrium heating rates. However, an increase in heating rate leads to a different DSC measuring curve [5]. The analysis and data interpretation of such DSC measurements is a major challenge.

In this paper, the relations between DSC descriptors (short-term determinations, which are based on physical test methods) and heating rates are presented using DSC-supported reheating tests of micro samples. DSC descriptors are characteristic features for microstructural changes derived from the temperature-dependent endo- or exothermic peaks of the DSC curve. The descriptors are quantified and analyzed depending on the heating rate.

Additionally, universal microhardness (UMH) measurements are carried out for evaluating the heat treatment states of the samples after the DSC measurements. This indentation method provides microhardness descriptors which enable a comparability for micro and macro samples and thus gives a validation feature for a calorimetric characterization with increased heating rates [6].

The aim of this investigation is to accelerate the DSC measurements regarding the high-throughput approach of the CRC 1232 without compromising the calorimetric results.

2. Materials and Methods

2.1. Materials

The experiments were carried out with spherical micro samples of bearing steel SAE52100 (German grade 100Cr6 or AISI 52100). The samples were separated from a cast wire and rolled into a spherical geometry with a diameter of 1 mm in a roller ball production process. The material used is a conventional, commonly used bearing steel which is available in spheres and similar sizes as the generated droplets of the future high-throughput process of the CRC 1232, allowing the validation of short-term characterization via descriptors. The microstructure of the samples directly after the manufacturing process consists of martensite with retained austenite and globular carbides (Figure 1a). After heat treatment in a standard vacuum furnace with a heating rate of 15 K/min from room temperature to 850 °C, holding for one hour at this temperature and then cooling with 8 bar nitrogen,

the microstructure of the samples changes to a mixture of retained austenite, perlite, globular cementite and globular carbides (Figure 1b).

Macro samples were turned from a rolled bar with a diameter of 20 mm into DSC samples with a diameter of 4 mm and a height of 1.5 mm. The etched sample shows a spheroidized microstructure with perlite and globular cementite (Figure 1c).

Figure 1. Microstructure of: (a) micro samples after roller ball production process; (b) micro samples after heat treatment; (c) macro samples; etched 25–30 s in 3% alcoholic HNO₃, all equatorial respectively longitudinal cut images.

The chemical composition of the samples is shown in Table 1. The chemical composition of macro samples is within the range of the DIN EN ISO 683-17:2000-04 standard except for sulfur. Even though the micro samples were produced within the same batch, their chemical composition can vary slightly due to sampling. Therefore, to represent the utilized micro samples, two random samples were examined and are presented here (Table 1). While sample ‘Micro Test 2’ slightly exceeds the threshold values of DIN EN ISO 683-17:2000-04 for carbon as well as for sulfur, the sample ‘Micro Test 1’ contains chrome and nickel values that are too low, whereas these values are at the upper threshold for sulfur and silicon.

Table 1. Chemical composition of the investigated alloys in wt % in comparison with the limitations of the DIN EN ISO 683-17:2000-04.

Material		Chemical Composition in wt %							
		Fe	C	Cr	Mn	Ni	P	S	Si
Macro (a)	-	bal.	1.00	1.45	0.29		0.013	0.023	0.25
Micro Test 1 (b)	-	bal.	1.03 (c)	1.20	0.38	0.40	-	0.015 (c)	0.35 (a)
Micro Test 2 (b)	-	bal.	1.07 (c)	1.31	0.35	0.17	-	0.018 (c)	0.35 (a)
DIN EN ISO	min		0.93	1.35	0.25	0.00	-	-	0.15
683-17:2000-04	max	bal.	1.05	1.60	0.45	0.40	0.025	0.015	0.35

(a) by optical emission spectroscopy (OES), (b) by atomic absorption spectrometry (AAS), (c) combustion analysis.

Since the micro samples were produced as standardized balls for ball bearings, it was not possible to produce the macro samples using the same melt. However, the macro samples are only needed to examine the scalability of relations of DSC descriptors and heating rates obtained in tests with micro samples. In this case, the differences in chemical composition and manufacturing processes, as well as different initial states of the microstructure do not play a decisive role.

2.2. Differential Scanning Calorimetry Measurements

Differential scanning calorimetry is one of the methods of thermal analysis, and is defined in DIN 51,005 as a generic term for the study of materials involving thermal control. In the process,

the chemical or physical properties of the analyzed material are measured as a function of time while subjected to a controlled temperature regime.

In the DSC method, there are two crucibles subjected to an identical temperature program. The thermal contact between the sample and the crucible is of particular importance. One crucible contains the investigated material and the other crucible contains a reference material of comparable heat capacity. If an endothermic or exothermic reaction takes place in the testing sample, the heat flow between the oven and the sample differs from the one between the oven and the crucible with the reference. Such temperature difference is the primary measurement signal. The heat flow rate is proportional to it [7].

The DSC experiments were carried out with a calorimeter of type HT TGA/DSC 3+ (© METTLER TOLEDO, Hamburg, Germany). Investigations were done with both low (10 K/min) and relatively high (70 K/min) heating rates under an argon atmosphere using an empty reference crucible. Calibration of the DSC was done by using five different calibration materials (indium, zinc, aluminum, gold and palladium) covering the desired temperature range with all used heating rates. The high heating rates and the usage of an empty reference crucible were applied to ensure high-throughput. The measured descriptors are onset, endset, and the area under the peak. The evaluation of the peaks is shown schematically in Figure 2.

Figure 2. Differential scanning calorimetry (DSC) descriptors: onset, endset and the area under the peak.

2.3. Universal Microhardness Measurements

Hardness is the measure of a material's resistance against mechanical penetration. Instrumented nano indentation measurements enable the examination of elastic and plastic material behavior during the whole indentation process without subsequent optical inspection of the remaining hardness indentation. Furthermore, in comparison to standard macro hardness testing, UMH measurements reveal very local results, since indentation sizes are small, evidently depending on material properties and indentation force. Therefore, minimum and maximum values of measurements of one sample contain information on the local microstructure.

For the investigations of the universal microhardness the samples were prepared by embedding and grinding to the equatorial plane. The surface of the samples was polished so that instrumented nano indentation measurements could be carried out. For the determination of the hardness, a Fischerscope H100C testing device with a Vickers indenter was used. The indentation force was set to 1000 mN. A loading time, holding time and relief time of each 10 s was used. For each sample, 25 individual UMH measurements in the center of the sample were made.

2.4. Experimental Parameters and Data Analysis

The samples were examined for their behavior when varying heat treatment parameters during DSC measurements. Austenitizing temperature (TA) and holding time (tA) were kept constant while heating and cooling rates were varied. The experimental parameters and the characterization methods are summarized in Table 2.

Table 2. Heating, cooling and austenitizing parameters.

Heating Rate K/min	TA °C	tA min	Cooling Rate K/min	Characterization Method
10	1000	20	30	DSC, UMH
30	1000	20	30	DSC, UMH
10	1000	20	50	DSC
30	1000	20	50	DSC
50	1000	20	50	DSC
70	1000	20	50	DSC

Evaluation of experimental data followed standard statistical methods. Since the relevant data follows a rational scale (equidistant values and temperature in K, thus an absolute point of zero is given), there are no restrictions in terms of applicability of mathematical operators. All displayed graphics show the arithmetic mean of relevant descriptors, that has been evaluated over sample sizes varying from $n = 3$ (for macro samples) to $n = 16$ (for micro samples).

Since a sample has to be embedded and polished for the microhardness measurement, it is not possible to perform a hardness–DSC–hardness experiment on the same sample. Therefore, the comparison was made between the arithmetic mean of hardness descriptors of four samples without heat treatment and of samples that have been subjected to varying heat treatments in DSC.

For the statistical analysis of UMH measurements, an arithmetic mean (together with a standard deviation) of the aforementioned 25 individual measurements per sample was computed and considered as microhardness value for this sample for future computations.

Comparisons were made between different heating rates, as well as the mass of samples per DSC measurements, i.e., one micro sample, three micro samples at a time, or one macro sample (Figure 3). As mass-relevant descriptors like area under the peak are already computed in relation to the sample mass, this finds no consideration in the data analysis when comparing those three variations.

Figure 3. The shape and approximate weight of the samples.

3. Results

3.1. Results of DSC Measurements

The spherical micro samples are very different from the optimal DSC samples. Both the low mass of about 2 mg, as well as the point contact with the crucible make the implementation and evaluation of measurements more complicated. In previous investigations, it has already been stated that the peaks of DSC curves of spherical micro samples are less pronounced than those of a flat macro sample [8]. In the heating part of the experiments with micro samples, two or sometimes three peaks are detected, while there is only one explicit peak in the cooling part. Increasing the heating rate

not only increases throughput, but also simplifies the evaluation of peaks, as they are more visible. In Figure 4, four example curves with heating rates of 10, 30, 50 and 70 K/min are shown. Hereinafter, peaks are identified by their number of occurrences. As mentioned above, during heating, three peaks can usually be detected, hence the numbers 1–3 will refer to the peaks of the heating phase, and as there was only one visible peak during cooling, this will be peak 4.

All experiments were performed with empty reference crucibles to accommodate the high-throughput method. Therefore, the measured DSC curves are not horizontal due to the difference of the heat flows between the reference and sample crucibles. The different heat flows are a result of thermal asymmetry between the sample and the reference crucibles because the heat capacity of the sample is not compensated by the reference. This effect has influence on the measured heat flow levels, but not on the transformation temperatures.

Figure 4. Example of heat flow curves of DSC measurements of micro samples for a heating rate of 10, 30, 50 and 70 K/min.

In Figure 5a,b, the start and end temperatures of the transformation peaks of one micro sample with varying heating rates (10, 30, 50 and 70 K/min) are displayed. The displayed values are arithmetic means of the results for $n > 7$ micro samples. Error rates in this graphic are standard deviations. Especially in Figure 5a, one can see that the transformation peaks for 10 K/min, 30 K/min and 50 K/min only differ slightly (less than one standard deviation), whereas the transformation peaks for 70 K/min have a much lower third peak during the heating process. Furthermore, the data clearly shows a significant decrease in standard deviation when it comes to the second peak (around 750 K). This is consistent throughout all heating rates, but grows with higher rates, as 50 K/min and 70 K/min have a higher standard deviation for the second peak than 10 K/min and 30 K/min.

Figure 5. Temperatures for start (a) and end (b) of transformation peaks computed as arithmetic mean over a sample size of $n(10 \text{ K/min}) = 13$, $n(30 \text{ K/min}) = 16$, $n(50 \text{ K/min}) = 14$ and $n(70 \text{ K/min}) = 8$.

An evaluation of the absolute value of the area under the transformation peaks shows that the standard deviation is extremely high in all measurements, with a heating rate of more than 10 K/min (Figure 6). To ensure the reproducibility of the data, a larger sample quantity is necessary. There is no consistent data trend visible, only transformation peak 1 shows an increase of the area under the peak with increasing heating rate.

Figure 6. Absolute value of the area under transformation peaks with varying heating rates. As in Figure 5, these are arithmetic means computed with a sample size $n > 7$.

The DSC curve of the macro sample has only one clearly visible transformation peak each in the heating and in the cooling part (Figure 7). During the heating part, only peak 2 (start (A_{C1b}) and end (A_{C1e}) of the transformation of ferrite into austenite) is visible. Peak 1 is recognizable only at the higher heating rate of 30 K/min. However, a correct evaluation of the peak is not possible.

Figure 7. Example of heat flow curves of DSC measurements of macro samples for a heating rate of 10 K/min and 30 K/min and a cooling rate of 30 K/min.

Figure 8 shows starting temperatures for all peaks for varying mass input, i.e., one micro sample (for 10–70 K/min), three micro samples (10–50 K/min) and one macro sample (10–30 K/min). Considering that macro samples only show one peak during heating and one peak during cooling, all three variations show similar behavior. The difference originating from mass yields no higher deviation than the one originating from different heating rates and is still less than a standard deviation. One difference is that macro samples only show one peak for heating (peak 2 of micro samples) and one for cooling (peak 4 of micro samples).

Figure 8. Onset temperature for varying heating rates (10, 30, 50 K/min) and mass input (one micro sample, three micro samples and one macro sample) computed as an arithmetic mean from $n > 3$ samples.

3.2. Results of UMH Measurements

There have been several experiments conducted to investigate the influence of a DSC treatment on hardness (described through eight different descriptors). Hardness descriptors were measured on micro and macro samples without heat treatment and on samples with different heat treatments in the DSC (heating rates of 10 K/min and 30 K/min). The Martens hardness (H_M), the hardness without elastic deformation (H_{Upl}) and the indentation hardness (H_{IT}) descriptors were investigated in more detail.

When evaluating hardness descriptors on one sample, it is necessary to compute the arithmetic mean over all 25 measurements. Figure 9 shows the resulting arithmetic mean and standard deviation for four different samples of the three hardness descriptors. The standard deviation is comparatively high, but the arithmetic means have similar values. There is no difference in hardness descriptors comparing samples that were measured in the DSC as a single micro sample and those that were measured in a set of three. The results were therefore regarded as equal in further analysis.

Figure 9. Arithmetic mean of hardness descriptors (25 measurements each) of four different micro samples and their standard deviations.

The difference in indentation hardness H_{IT} , as an exemplary hardness descriptor, between the DSC measurement at 10 K/min and the one at 30 K/min was very small in comparison to the indentation hardness without heat treatment (Figure 10a). For macro samples as well as for micro samples, a higher heating rate seems to result in lower values of hardness descriptors. This effect is significantly higher for micro samples than for macro samples (Figure 10b).

Figure 10. (a) Hardness descriptors of micro samples with different heat treatments in the DSC; (b) relative change in hardness descriptors when varying the heating rate of DSC from 10 K/min to 30 K/min of micro and macro samples.

4. Discussion

According to the results of the investigations carried out, the critical heating rate for the spherical micro samples is between 50 and 70 K/min. This is mainly due to the maximum sampling rate of ten measured data per second. As the heating rate increases, fewer measured data are taken, reducing accuracy. As a result, some peaks are not displayed correctly, which makes the evaluation of the curves that were recorded at 70 K/min particularly difficult. On all curves except those with a heating rate of 70 K/min, three peaks can be detected. Thus, with the fastest heating rate curve, only A_{C1b} and A_{C1e} can be determined. However, these transformation points can be determined at all heating rates, with the lowest standard deviation of maximal 3 °C. DSC results for the start of ferrite into austenite transformation A_{C1b} are in agreement with the expected temperature of 751 °C shown in the continuous TTA diagram of 100Cr6 for low heating rates [9]. The changes in intensity of peak 1 can be explained by the amount of retained austenite or the formation of chrome carbides. Due to the slightly different initial microstructure of the micro samples, transformation occurs between 330 and 360 °C during heating.

Neither the small mass of the spherical micro samples, nor the point contact with the crucible, have any effect on the accuracy of the measurement of the transformation temperatures. Thus, an increase in the amount and thus also the mass of micro samples from one (2 mg) to three pieces (6 mg) leads to no improvement in accuracy. The results of the measurements on the micro samples are comparable with the measurements on flat macro samples with a mass of about 95 mg. However, the low mass of about 2 mg has an extremely high influence on the reproducibility of the evaluation of the area below the peaks.

After the heat treatment of the micro samples in the DSC, the measured hardness descriptors decrease in comparison to the samples without heat treatment due to the slow cooling rate of 30 K/min, which leads to a ferritic-perlitic microstructure, as no martensitic hardening can be obtained, e.g., the indentation hardness H_{IT} drops from 10.1 GPa for the initial martensitic microstructure to 2.6 GPa after DSC heat treatment with a heating rate of 10 K/min.

UMH measurements provide a very local material characterization depending on the position of indentation and therefore include a high possibility of detecting supposedly opposite information on hardness within one sample. Exemplarily, the indentation hardness H_{IT} of one micro sample based on 25 measurements after heat treatment in the DSC at a heating rate of 10 K/min varies between 1.79 GPa (minimum value) and 3.29 GPa (maximum value), while the calculated mean is 2.61 GPa (Table 3). Depending on the inspected phase, the indentation hardness can be relatively low for perlite-ferrite on the one hand and very high for precipitated carbides on the other. Since the microstructure of the micro samples shows a high occurrence of carbides the scattering is expected to be high. Despite the high standard deviations for UMH measurements of one micro sample (Figure 8), comparability between several samples is ensured by the low standard deviations of the averaged mean value, which underlines the validity of the method.

Table 3. Minimum and maximum values of the indentation hardness H_{IT} of micro samples after the heat treatment in DSC with a heating rate of 10 K/min.

Sample Number	Indentation Hardness H_{IT} (GPa)		
	Minimum	Maximum	Difference
1	1.79	3.29	1.49
2	1.92	3.34	1.42
3	1.74	3.28	1.54
4	1.91	3.67	1.75
Mean	1.84	3.39	1.55

The hardness varies only slightly between the two investigated heating rates of 10 K/min and 30 K/min, which is due to the constant holding time of 20 min after heating and the resulting

approximately equal diffusion time. Therefore, as expected, the main influence on the hardness is not the heating rate, but the cooling rate during the heat treatment. Nevertheless, a tendency towards lower hardness descriptor values with increasing heating rate is noticed. In comparison, micro samples with their low weight are more sensitive to accelerations of heating speeds than macro samples. The relative change of indentation hardness H_{IT} is ten times higher than for macro samples (Figure 10b).

5. Conclusions and Outlook

The sudden drop of temperature for DSC peaks for a heating rate of 70 K/min confirms the expectation that there is a critical maximum heating rate for DSC measurements. The realization of DSC measurements with a high heating rate is beneficial for the high-throughput material development in the CRC 1232. Therefore, heating rates above 50 K/min will be examined in detail in further investigations in order to find such a critical maximum heating rate. Furthermore, UMH measurements are planned to investigate the corresponding indentation hardness.

Since the hardness descriptors only slightly vary for different heating rates (of 10 K/min and 30 K/min) of the heat treatment during DSC measurements, this needs to be examined for further heating rates; therefore, further investigations with heating rates of, e.g., 50 K/min (or higher) are planned. As discussed, the heating rate has no significant impact on the indentation hardness, as in this study the diffusion time approximately remained unchanged due to the constant holding time. Additionally, the hardness is expected to change with varying cooling rates. To determine whether the decisive influencing parameter on the indentation hardness is the cooling rate or the missing holding time, these influences will be examined in further investigations.

Author Contributions: A.T. performed DSC experiments and wrote the paper by the aid of H.S. in questions of UMH and C.P. in questions of data analysis. A.v.H. and R.D. supervised all investigations and supported with their expert knowledge. The CRC 1232 ‘Farbige Zustände’ contributed the investigated materials.

Funding: This research was funded by the German Research Foundation (DFG).

Acknowledgments: Financial support of subprojects U03 “Thermal and thermomechanical heat treatment”, D01 “Qualification of material conditions with mechanical and physical measuring methods” and P02 “Heuristic, statistical and analytical experimental design” of the Collaborative Research Center CRC 1232 by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)—project number 276397488—SFB 1232 is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Ellendt, N.; Ciftci, N.; Goodreau, C.; Uhlenwinkel, V.; Mädler, L. Solidification of single droplets under combined cooling conditions. *IOP Conf. Ser. Mater. Sci. Eng.* **2016**, *117*, 012057. [[CrossRef](#)]
2. Drechsler, R.; Eggersgluß, S.; Ellendt, N.; Huhn, S.; Mädler, L. Exploring Superior Structural Materials Using Multi-Objective Optimization and Formal Techniques. In Proceedings of the 6th IEEE International Symposium on Embedded Computing and System Design, Patna, India, 15–17 December 2016.
3. Ellendt, N.; Mädler, L. High-Throughput Exploration of Evolutionary Structural Materials. *HTM J. Heat Treat. Mat.* **2018**, *73*, 3–12. [[CrossRef](#)]
4. Morra, P.V.; Böttger, A.J.; Mittemeijer, E.J. Decomposition of iron-based martensite—A kinetic analysis by means of DSC and dilatometry. *J. Therm. Anal. Calorim.* **2001**, *64*, 905–914. [[CrossRef](#)]
5. Kefßler, O.; Milkereit, B.; Schick, C. Zeit-Temperatur-Auflösungs- und Zeit-Temperatur-Ausscheidungs-Diagramme von Aluminiumlegierungen. *Fortschritte in der Metallographie* **2012**, *44*, 3–12.
6. Lucca, D.A.; Herrmann, K.; Klopstein, M.J. Nanoindentation: Measuring methods and applications. *CIRP Ann. Manuf. Technol.* **2010**, *59*, 803–819. [[CrossRef](#)]
7. Frick, A.; Stern, C. *DSC-Prüfung in der Anwendung*, 2nd ed.; Carl Hanser Verlag: München, Germany, 2013; pp. 45, 49–51.

8. Cramer, L.; Toenjes, A.; Steinbacher, M.; von Hehl, A.; Zoch, H. Dilatometric and Calorimetric Short-Term Characterization Methods on 100Cr6 Micro Samples for High-Throughput Investigations. *Adv. Eng. Mater.* **2018**. [[CrossRef](#)]
9. Orlich, J.; Rose, A.; Wiest, P. Zeit-Temperatur-Austenitisierung Schaubilder. In *Atlas zur Wärmebehandlung der Stähle*; Verlag Stahleisen m.b.H.: Düsseldorf, Germany, 1973; Volume 3.

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).