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ADVANCED MATHEMATICAL TREATMENT OF DILATOMETRY AND CALORIMETRY TO DISCRIMINATE AND QUANTIFY MULTIPLE PHASE TRANSFORMATIONS

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Abstract

Dilatometry and calorimetry are well-established techniques, and have been used successfully for decades; however, they are seldom used to quantify the progress of a transformation. Most often, these techniques are used to detect start and finish of transformations. When used quantitatively, current analysis of dilatation data does not account for the different changes in density for the multiple transformed phases. Similarly, quantitative calorimetric analysis does not account for different rates of enthalpy release for different transformed phases. The technique proposed for both dilatometry and calorimetry consists on posing a differential equation based on dilatation or temperature data generated under controlled experimental conditions. When integrated, this equation extracts phase fraction evolution from the experimental data. Like all differential equations, the equation posed involves coefficients and integration constants. The work presented differs from other similar work in that the coefficients are obtained from calibration before, after, and at transition points for each transformation, with a minimum of need of previously tabulated data. The mathematical treatment will be introduced, and applications will be discussed involving solid-state precipitation in Al-Ag, precipitation during solidification in A356, martensitic transformation in creep-resistant steel, and bainitic and martensitic transformation in 4140 steel.

Introduction

Cooling curve analysis (CCA) has been discussed in the literature for a long time and has reached a high degree of progress [1, 2, 3, 4, 5, 6]. Recent developments in CCA have led to expanding this versatile method to the proper treatment of multiple simultaneous phase transformations [1]. This paper summarizes the CCA methodology for single and multiple phase transformations. Similar to previous CCA techniques, the methods in this paper rely on measuring the temperature of a sample as it undergoes phase transformations during Newtonian cooling. The proposed CCA methods can work under a variety of cooling conditions [1, 3], they require little to no specialized machinery, facilities, computing power and they are timesaving. These benefits are more evident when considering that these types of measurements are currently made using techniques that are either slow, expensive or difficult to access, and in some cases, unable to accommodate realistic sample sizes or cooling rates; among those one can mention microscopy [7], differential scanning calorimetry (DSC) [7, 8, 9, 10], differential thermal analysis (DTA) [11, 12], synchrotron diffraction [13], dilatometry [14, 15] or indirect measurements such as density [16], magnetic field [17] and electrical resistivity [18]. The limitations of these techniques are discussed in [4].

Dilatometry is a well-established technique primarily used to study the response of a material to temperature change [19]. The data obtained from a dilatometer is used to calculate the start and finish temperatures of the transformation(s). American Society for Testing and Materials (ASTM) has developed a well-known method (informally called the *lever-rule* method) for quantifying the fraction of a forming phase from dilatation data [20]. However, this method assumes the progression of the phase transformation is linear with dilatation [21]. In addition, this standard method bundles all simultaneous transformations as if a *single phase transformation* took place and the parent phase transformed into a homogeneous phase. This is rarely the case in most materials specifically steels continuously cooled after austenitizing [22].

Much work has been done towards a better analysis of dilatometry data to better predict the phase fractions in materials which undergo multiple phase transformations. Onink et. al. pioneered models for quantifying the phase fractions in multiple phase transformations in Fe-C steels [23]. Their models are based on the lattice parameters of the constituting phases and their dependence on temperature and composition. Many researchers have built on the analysis presented in [23] and tried to expand them to take into account alloying elements [24, 25, 26], and diffusionless phase transformations (e.g. formation of martensite and bainite from austenite) [27, 22, 28, 29]. De Andres et. al. have developed a model on the basis of lattice parameters for the decomposition of pearlite to austenite in an eutectoid steel upon heating [30]. Other researchers have taken a different approach and used the density of the constituting method with expressions for the phase densities as a function of temperature and composition to predict the austenite fraction in austenitization of a low carbon steel [32]. Avrami-type mathematical expressions are also used in some literature to quantify the transformation kinetics in low carbon steels [33, 14].

All of the work discussed in the previous paragraph is finely tuned for specific alloy systems (mainly low alloy and low carbon steels) and are rarely applicable to the broader group of materials. In addition, most of the models suffer from limiting assumptions (e.g. geometrical assumptions, equilibrium estimations for non-equilibrium transformations, limited number of alloying elements, etc.) that hinder their application to all phase transformations.

The goal of both dilatometry and CCA is to obtain phase fraction evolution information of a material as it undergoes heating or cooling. Because of the similarities in the results and sample conditions during the experiment, dilatometry and CCA can be seen as complementary techniques. The primary difference between the dilatometry and CCA is that the dilatometry model is based on the length of the sample, which is measured directly, whereas CCA is based on the temperature of the sample, which must be processed by using a heat transfer model [34].

Our research group has been pioneering rigorous analysis techniques that so far have yielded important results. A compilation and discussion of the state of progress will be presented in the following sections.

Experimental

The experimental conditions and setup for all calorimetry experiments are described in [1, 2, 3, 4]. For the dilatometry investigation, a vertical Linseis RITA L78 high speed quenching dilatometer at the Canadian Center for Welding and Joining (CCWJ) was utilized for multiple

phase transformations and a Bahr DIL-805/D dilatometer at the institute of joining and assembly (IJA) in Germany was used for single phase transformation analysis [34]. The materials investigated for calorimetry consisted of different aluminum alloys (pure aluminum, 413, 356, 380) [2, 3], Al-Ag alloy [4], and aluminum A356 (simultaneous solidification-precipitation) [1]. The dilatometry analysis was carried out on AISI 4140 and 9Cr3W3CoVNb steel samples [34].

Results and Discussion

Research on calorimetry includes the analysis of a single phase transformation, either to full completion where the parent phase is completely transformed into a new phase, or partial transformation. The analysis of multiple simultaneous phase transformations with different start and end times has also been studied.

Research on dilatometry includes a proposed integration methodology aiming to obtain the best practical quantification of phase fractions during a single transformation, comparing this methodology to calorimetry and traditional dilatometry analysis, extending the integration methodology to multiple simultaneous phase transformations, the analysis of a single phase transformation, either to full completion where the parent phase is completely transformed into a new phase, or partial transformation. The analysis of multiple simultaneous phase transformations with different start and end times have also been studied.

CCA for single transformation e.g. $liquid \rightarrow solid$

This methodology only requires the time-temperature data from a sample which is being cooled freely to output the phase fraction of the forming phase. This method does not require any additional information about the material or phases involved. Examples of this methodology are solidification $(L \rightarrow S)$ and austenite to martensite transformation. The step by step development of this methodology can be found in [2, 3]. Single transformation CCA analysis has been applied to the solidification of different aluminum alloys to find the solid fraction as shown in Figure 1[2].



Figure 1: Solid fraction curves for commercially pure P1020, 356, 380 and eutectic 413 aluminum alloys obtained from single transformation CCA analysis adapted from [2].

CCA for multiple transformations e.g. $liquid \rightarrow solid + precipitates$

Recent advancements in CCA allows for separation of complex simultaneous phase transformations such as precipitation during solidification in aluminum alloys or potentially for the austenite to pearlite/martensite/ferrite transformation in steels. Unlike the previous single transformation methodology, this new approach requires some thermodynamic data relating to the final phases (i.e. latent heat of some phases). This information can easily be obtained from standard thermophysical tables or calculated using commercial software such as Thermo-Calc. One very appealing potential application of the proposed methodology is in the welding of pipeline microalloyed steels (e.g. X70, X80 and X100). The step by step development of this methodology can be found in [1, 4]. Aluminum A356 was used to demonstrate the application of multiple transformation CCA analysis. This aluminum alloy shows precipitation of Mg_2Si and $Al_8FeMg_3Si_6$ during solidification. Figure 2 shows the separated evolution curves for the solid aluminum matrix and the precipitates with temperature [1]. To further show the application of this methodology, an Al-45 wt%Ag alloy was separately studied [4]. This alloy demonstrates precipitation of Ag_2Al during solidification. Figure 3 displays the evolution of the Ag_2Al precipitate fraction with temperature.



Figure 2: Evolution of phase fraction versus temperature forming in aluminum A356 alloy during solidification for (a) solid aluminum matrix (b) precipitates. Results from multiple transformation CCA analysis adapted from [1].

Dilatometry for single transformation e.g. $\gamma \rightarrow martensite$

This methodology uses raw dilatation-temperature data obtained from a dilatometer to calculate the phase fraction of the forming phase. This method does not require any additional information about the material or phases involved. Examples of the application of this methodology



Figure 3: Fraction of Ag_2Al precipitated in an Al-45 wt%Ag alloy adapted from [4].

can be found in [34] in which the formation of martensite from austenite in 9Cr3W3CoVNb steel is analyzed. Figure 4 contains the single transformation dilatometry analysis and compares it to CCA and experimental calculations.



Figure 4: Martensite fraction in 9Cr3W3CoVNb steel from single transformation dilatometry analysis compared to CCA and the values from the ASTM standard adapted from [34].

Dilatometry for multiple transformations e.g. $\gamma \rightarrow bainite + martensite$

In the case of multiple simultaneous or sequential phase transformations, a more complex approach is required. Similar to its counterpart in calorimetry, this new approach requires some material property data relating to the final phases (i.e. density at room temperature of some phases). A very useful example of this methodology is austenite decomposition into multiple phases such as ferrite, pearlite, bainite and martensite. The proposed methodology can be used to better quantify all phase transformations. Specifically in steels, this methodology can help improve the quality of CCT diagrams by adding valuable information to these diagrams that could not be included with previous methods of analysis. AISI 4140 steel was cooled at 1.5 K/s from 1223 K. This results in the simultaneous formation of bainite and martensite from austenite. Figure 5 shows the separated evolution of the bainite and martensite fraction.

Summary

The integration methodology developed for the analysis of cooling curves and dilatometric data has been tested successfully in a broad range of materials: commercially pure P1020, 356, 380



Figure 5: Evolution of phase fraction versus temperature in AISI 4140 steel from multiple transformation dilatometry analysis for (a) bainite (b) martensite.

and eutectic 413 aluminum alloys [2], 10 variations of cast aluminum A356 alloy [1], Al-45%Ag [4], 9Cr3W3CoVNb steel [34], and AISI 4140. It is reasonable to expect this methodology to be applicable in many other materials of practical significance, limited only by the sensitivity of the measurement technique for complete single transformations. For example, small amounts of precipitation might be difficult to quantify.

For partial transformations or multiple transformations, additional data is necessary: thermodynamic data and (in some cases) quantitative metallography for CCA, and density data for dilatometry. In some cases, the needed data can be obtained from analysis of samples of the same material at different cooling rates such that the transformations become complete, or a multiple transformation problem turns into a single transformation one.

In the case of calorimetry, cooling rate and size of the sample are related, and attention must be paid to experiment design. For both calorimetry and dilatometry, sample temperature homogeneity must be considered carefully. In the experiments discussed above, the Biot number was always small, ensuring temperature homogeneity. In addition, there were no longitudinal gradients such as those often present in Gleeble testing.

One of the advantages of the integration procedure proposed, is that it can be extended to problems beyond those tested. In both calorimetry and dilatometry, analysis during heating is possible; for dilatometry this is trivial, but for calorimetry this involves the use of furnaces (either convective or radiative) and might have limitations in practice. The analysis of steels during heating is especially relevant currently because of the fast growth of laser heat treatments, in which there is ample (circumstantial) evidence that full austenitization (Ac₃) is reached at temperatures significantly above the thermodynamic value (A₃).

For the case of CCA, different well known boundary conditions can be treated rigorously. For sand casting, the heat transfer model would be based on Chvorinov's analysis instead of constant effective heat transfer coefficient. Cooling by radiation and combined radiation and convention can also be tackled. The application of CCA to sand casting, although possible in theory, has not been implemented successfully. It is thought that shrinkage can greatly affect the part/mold heat transfer parameters. Also, possible phase transformations in the sand might play a role. Future work on this area would be of significant practical value to casting operations. CCA substituting convection for conduction has the potential of creating a whole CCT diagram in a single Jominy test. This is the focus of current research in our group. Other possible extensions of CCA would bring an additional quantification of phase fractions to systems in which it is currently not practical to measure phase fraction; hot stage microscopy and welding are among such systems.

For the case of dilatometry, the multiple transformation methodology in development should be able to yield light into simultaneous transformations in steels. Typically simultaneous transformations are treated as if they were sequential and with similar density change, not simultaneous and with products of varying densities. Proper quantification of phase fraction also provides control over the criterion to determine the start and finish of transformations. Instead of the traditional intersection of tangents (which any practitioner will recognize it can carry subjectivity at times), a clearly designated criterion for start and stop based on percentages such as 1%, 5%, 99%, etc. is possible.

For transformations such as martensite in steels, in which completion is occasionally reached well below room temperature, the determination of the end of the integration is occasionally not well defined. In these cases quantitative metallography is needed. What is remarkable, however, is that nearing the completion of the transformation, conditions resembling full transformation are typically present, allowing proper quantification (provided metallography of the sample is performed after testing). This convenient phenomenon is present in the traditional analysis of dilatometry too, and often used. It is worth to highlight that the wealth of data brought by the integration proposed comes at very little incremental cost over the traditional tests. The system used for the solidification alloys is described in detail in [3], and no hardware modifications are needed for the enhanced analysis of dilatometry.

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