Semi-solid processing and its as yet unexplored potential

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Abstract. Thanks to the available advanced control technology, manufacturing processes which have been described in the past but their hidden potential remained untapped are now continuing to be developed. As a result, even conventional materials which have been around for years can be manipulated to obtain unusual microstructures with specific mechanical and physical properties. Semi-solid processing belongs to the above-described group: it had been studied in the past but, due to complicated process control, it gradually lost its appeal. However, advanced techniques of temperature field control enable engineers to control this complex process accurately. One of the innovative methods of semi-solid processing is mini-thixoforming. As it focuses on very small-size products, it offers very steep heating curves and extremely high solidification and cooling rates, when compared to conventional thixoforming. The capabilities of this process were tested on X210Cr12 ledeburitic tool steel. After the optimum processing conditions were found, additional materials were tried, ranging from low-carbon microalloyed steels through medium-alloy steels to high-alloy tool steels. The microstructure evolution upon the mini-thixoforming process is an issue of its own. The final microstructure of X210Cr12 consisted of more than 90 % of austenite and chromium carbides. Semi-solid processing of a steel with a high vanadium content led to a microstructure comprising MA matrix and globular vanadium carbides. In a low-alloy steel, martensitic microstructure was obtained.

Keywords: semi-solid state, thixoforming, rapid solidification, tool steel

1. Introduction
Increasing demands on materials properties drive the development of new processing routes for both metallic and non-metallic materials. Thanks to these routes and innovative procedures, attractive mechanical properties can be obtained, even in materials which used to be processed mostly by conventional techniques. One of the interesting paths to obtaining attractive properties is semi-solid processing [1]. This technique offers wide opportunities for producing non-traditional microstructures and enables some difficult-to-form materials to be processed. The forming process involves either one or a very few forming operations, and therefore delivers significant time savings and contributes to cost-effective production. In addition, it can produce intricate-shape products. Two routes are available when thixotropic behaviour is desired in a material [2,3]. These comprise thixoprocessing and rheoprocessing [4]. Thixoprocessing involves materials which are first melted, and then cast and let solidify. After that, they are reheated to the semi-solid range and formed. In rheoprocessing, the material is cooled down to the semi-solid state and then formed. Rheoprocessing is thus more energy-efficient, as it does not require reheating to the semi-solid state. On the other hand, it places much greater demands on the process technology and control, which is why it is less common than thixoprocessing. The shared characteristic of both processing routes is the thixotropic behaviour of the metal. Thixotropy is a deformation behaviour which is defined by a decrease in viscosity with increasing shear rate and time in semi-solid state. The shear stress and deformation in the semi-solid
material during forming cause the material’s viscosity to decrease [5]. The required forming force is relatively low when compared to the forces needed for conventional processes. Optimum thixotropic behaviour following heating to the semi-solid state should occur when the solid fraction is between 10 and 60 %, depending on the particular semi-solid processing route [6]. For this reason, alloys which are less sensitive to the solid fraction are better candidates for thixoforming, as they are less likely to solidify undesirably while they cool during die cavity filling. With them, the forming temperature is easier to control, which is a key aspect. Over the years, various semi-solid processing techniques have been developed. They became known as SSM (Semi-solid Metal Forming) processes. Among them, there are rheocasting, thixocasting, thixomoulding, thixoforging, thixoextrusion and thixorolling. In recent years, the research centre developed a semi-solid forming process which is termed mini-thixoforming [7]. Although the volume of the metal processed by this technique is small, the inherent problems with heating, namely the temperature field uniformity and temperature control accuracy, have been eliminated, thanks to an unconventional solution [8]. It led to successful processing of steels whose processing had been impossible to control due to narrow temperature intervals and high forming temperatures. In earlier experiments, X210Cr12 tool steel had been employed. The material is widely used for experimental semi-solid processing thanks to its wide freezing range which lies lower than those of other steels. In addition, a specific microstructure has been obtained thanks to particular thixoforming conditions in this otherwise ledeburitic steel. This microstructure consisted of polyhedral austenite grains embedded in carbide network. The austenite fraction exceeded 90 % [9]. Nevertheless, the question remained of how the microstructure would evolve upon semi-solid processing in other steels which are less commonly used for thixoforming. The purpose of the present experiment was to explore the capabilities of the thixoforming process and the microstructural evolution in a wider range of material from low-carbon high-alloy steels to high-alloy powder tool steels.

2. Experimental Programme

2.1. Selection of experimental materials
Based on literature search and calculations, X5CrNiCuNb16-4 precipitation-hardenable martensitic stainless steel stabilized with Nb was chosen as the experimental material. This material is a representative of the group of low-carbon high-alloy materials (Table 1). The steel chosen from the medium-carbon group was the microalloyed 30MnVS6 (Table 1). This steel, alloyed predominantly with manganese and silicon, is typically used for making forged parts. Another experimental material was the high-alloy CPM 15V steel. It contains a large amount of hard vanadium and chromium carbides which can be expected to remain stable and present in the microstructure during processing. The high-alloy steel CPM REX 121 was the last experimental material chosen. Of all materials selected, this had the highest carbon level. In addition, it contained almost 10 % vanadium. It had high tungsten and cobalt levels and an increased molybdenum content. As it has high levels of alloying elements and is manufactured by powder metallurgy, it belongs to materials which are difficult-to-form by conventional techniques.

### Table 1. Chemical composition of the experimental materials

| Material       | C    | Si   | Cr   | Ni   | W    | Co   | Cu   | Mn   | V    | Mo   | Nb   | P    | S    | Al   | Ti   |
|----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| X5CrNiCuNb16-4 | 0.024| 0.27 | 15.9 | 4.47 | -    | -    | 3.20 | 0.89 | 0.21 | 0.2  | 0.023| 0.018| -    | 0.11 |
| 30MnVS6        | 0.31 | 0.62 | 0.20 | 0.02 | -    | -    | 0.03 | 1.50 | 0.098| 0.007| -    | 0.018| 0.024| 0.02 | 0.026|
| CPM 15V        | 3.4  | 0.9  | 5.25 | -    | -    | -    | 0.5  | 14.5 | 1.3  | -    | -    | -    | -    | -    | -    |
| CPM REX 121    | 3.42 | -    | 3.99 | 9.75 | 8.71 | -    | 0.51 | 9.18 | 5.21 | -    | -    | -    | -    | -    | -    |

In order to develop a particular semi-solid processing route, one needs to map a number of materials parameters across the entire temperature range of the process. In this case, the required parameters were calculated using the JMatPro software because the exact values are very difficult to determine experimentally [11]. The dependence of liquid fraction on temperature plays a key role (Figure 1). The melting curves clearly show the differences among the materials in the semi-solid state. The most
favourable properties for thixoforming were found in the CPM REX 121 steel, where the increase in the melt fraction is almost linear. In addition, its freezing range is at lower temperatures than in the other steels. Based on the preliminary calculation, the suitable forming range for the CPM REX 121 steel was identified as 1200 – 1230 °C. The X5CrNiCuNb16-4 steel offers a relatively favourable freezing range as well. According to the calculated data, the forming range is between 1390 and 1415 °C. The K190 steel exhibits more problematic characteristics, as its increase in liquid fraction is steep. The suitable temperature interval is 1240–1255 °C. The most difficult one is the CPM 15V steel. Here, an increase in temperature of a mere 18 °C results in 90 % of melt in the material. The temperature interval suitable for forming is narrower than 10 °C, which places extreme demands on the temperature field control.

![Figure 1. Calculated theoretical liquid fraction vs. temperature](image)

Semi-solid processing was carried out using the mini-thixoforming process which involves forming in a closed die cavity and cross-extrusion [10]. The cross-section of the die cavity was 1.9×5 mm and its length was 20 mm. From all steels, stock of 48 mm length and 6 mm diameter was prepared. Their ends were cone-shaped in order to facilitate the passage of the heating current and to align the piece inside the shot sleeve. The stock was heated directly in the shot sleeve. The need for handling a melted workpiece was thus eliminated. High deformation speed is important to the semi-solid forming process, as the material must not solidify before it fills the die cavity. Therefore, the mean stroke velocity was 1 m/s. In the course of the forming process, the temperature was continuously measured with a thermocouple and regulated. As the initial forming temperatures were only determined on the basis of the materials’ chemical composition, the actual appropriate forming temperatures for all materials had to be found experimentally by iteration.

3. Results and discussion

Based on calculation, a forming temperature of 1400 °C was chosen for the X5CrNiCuNb16-4 material. The feedstock was heated to this temperature in 55 seconds. It was then held for 5 seconds to homogenize the temperature. The first experiments with the calculated parameters did not lead to complete filling of the cavity. The proposed temperature of 1400 °C was too low. The shape and other features of the feedstock showed that the liquid fraction was less than 10 %, the percentage normally reported as sufficient for the thixotropic behaviour to occur. In subsequent trials, the temperature was increased in steps of 5 °C. Finally, forming in the range of 1435 – 1445 °C proved optimal. In this temperature interval, the die cavity filled completely.

For the 30MnV86 steel, the chosen heating temperature was 1460 °C. In this case, the calculation proved very accurate, as the optimum forming range found by experiments was 1450–1460 °C.

CPM 15V had the narrowest available temperature interval of all the experimental materials. Its initial chosen temperature was 1305 °C. At this level, the liquid fraction was expected to be approx. 30 %. The feedstock, however, melted in the process, which showed that the temperature was too
high. Each next trial temperature was therefore 5\(^\circ\)C lower than the last. In this manner, the heating temperature was decreased in steps to 1265 \(^\circ\)C. After the heating trials with zero axial force, schedules with pre-defined amounts of compressive deformation were tested as well. Based on deformation force plots, the optimum forming range for the CPM steel was found to be 1265 – 1270 \(^\circ\)C.

The first processing temperature chosen for trials on the CPM REX121 steel was 1215 \(^\circ\)C. The outcome showed that at this temperature the liquid fraction required for adequate fluidity was not reached. By raising the heating temperature in steps of 5 \(^\circ\)C, the liquid fraction increased and the entire die cavity was filled eventually. The resulting product had the desired surface quality. The die cavity only filled completely at the temperature of 1235 \(^\circ\)C.

The effects of semi-solid processing were explored using metallographic analysis. Optical and electron microscopic observation showed that the single-phase microstructure of ferrite, a solid-solution phase, was retained after semi-solid processing of the X5CrNiCuNb16-4 material (Figure 2). In order to confirm this, diffraction phase analysis was carried out. According to the measured data, the ferrite fraction was 90 %. Another phase identified was austenite. Its amount of 5.5 % was just above the reported 5 % detection limit of the method. The remaining two phases, CrSi and Cr3Si, were present in amounts corresponding to the measurement error. Chemical homogeneity of the products was checked using EDS microanalysis because diffusion in semi-solid state is very rapid due to high temperature and under such conditions, phase or chemical segregation might occur. Chemical microanalysis only proved a slight increase in Cu concentration along grain boundaries. It can be attributed to its migration from the solid phase to the melt upon partial melting. The distributions of other elements were uniform. This is in agreement with the hardness readings of 340±2.3 HV which were identical before and after the processing. The above findings show that the rapid removal of heat did not lead to precipitation which is otherwise common in steels of this type at relatively low temperatures.

In the 30MnVS6 steel, the initial microstructure consisted of ferrite and pearlite. The processing produced a hardening microstructure, a mixture of martensite and bainite which is a relatively uncommon microstructure in semi-solid processed materials (Figure 2). As a result, the hardness of the material increased from 235 HV to 760 HV.

![Figure 2. Left: resulting microstructure of X5CrNiCuNb16-4 steel; right: 30MnVS6 steel](image)

The mini-thixoformed CPM 15V contained globular vanadium carbides embedded in an austenitic-martensitic matrix. This is in agreement with the results of diffraction phase analysis. The resulting microstructure contained 50 % austenite and 30 % dispersed martensite. High-stability V_{8}C_{7} carbides resisted melting during semi-solid processing and made up 20 % of the structure. Carbides with greater chromium content melted completely and their elements formed a eutectic, predominantly on grain boundaries (Figure 3). In the initial condition, the average measured hardness was 298 HV10. Upon thixoforming, its hardness was 728 HV10, which is a 2.5-times higher value. This increase can
be attributed mainly to the formation of martensite within the matrix and to the chromium precipitates in the form of network.

Figure 3. Left: resulting microstructure of CPM REX 121 steel; right: CPM 15V

The microstructure of the product of CPM REX 121 consisted of complex carbides and austenitic matrix and a small fraction of martensitic needles (Figure 3). Primary chromium carbides with sizes below 1 µm partially melted and transformed into a eutectic located at austenite grain boundaries. Its volume fraction increased slightly with the processing temperature. Complex V-W-Mo carbides, on the other hand, retained their initial character. In some cases, multiple carbides coalesced into larger particles. Changes at boundaries of large carbides took place. Those became more spherical than in the initial condition which is evidence of their partial melting. Using diffraction analysis, a 35 % fraction of austenitic matrix and 10 % fraction of martensite were found. The balance consisted of carbides. The largest share of those (35 %) had the M₈C₇-type carbides, in which the dominant element was vanadium. Minority fractions were represented by Mo₂V₄C₅ and Cr₁₂FeV₂. By contrast, CPM REX 121 showed the highest initial hardness, 407 HV10, of all materials. It had a high carbon content and, consequently, high volume fraction of martensite upon processing. This led to a notable increase in hardness to 830 HV10, which is the highest final value among all the materials compared. A contribution to this increase can be attributed to high levels of alloying elements, and thus a high proportion of undissolved carbides in the microstructure.

4. Conclusion
The present experiment involved mini-thixoforming of steels with various levels of carbon and alloying elements. Thanks to a close control of the entire process, the die cavity filled completely with all the materials. It was found that alloyed steels with higher carbon levels have microstructures which consist of the M-A constituent matrix and carbides whose shapes and distributions in the matrix depend predominantly on their chemistries. Owing to their high melting point, vanadium carbides retain their initial form. Chromium carbides, on the hand, melt partially and precipitate in the form of a eutectic. Steels with high chromium and low carbon levels exhibit single-phase structures with dissolved chromium. Thanks to the high level of chromium in solid solution, they can be expected to exhibit excellent corrosion resistance. By contrast, materials with lower level of alloying elements form hardening microstructures. Using this route, finished products with final microstructures and high strengths can be produced.

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