

Article

Martensite Transformation in Tool Steels under Isostatic Pressure—Implementation of In-Situ Electrical Resistivity Measurements into a Hot Isostatic Press with Rapid Quenching Technology

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Abstract: Powder metallurgical (PM) parts usually benefit from more homogenous and finer microstructures as opposed to conventionally processed material. In particular, hot isostatic pressing (HIP) combined with near-net-shape technologies can produce almost defect free PM tools with complex geometries. Recent advances in the plant technology of smaller HIP units allow the integration of hardening heat treatments in HIP processes. Thus, additional processing steps, transportation, energy consumption and cost are reduced. However, it is known that high pressure influences phase stability and transformation temperatures. Still, knowledge of the martensite start temperature (M_S) is crucial for the design of hardening heat treatment. Since the influence of pressure on M_S in HIP heat treatment is insufficiently investigated, it is the aim of this study to deploy a measurement method that allows to record M_S as a function of pressure, temperature and cooling rate. Taking the hot working tool steel AISI H11 (X37CrMoV5-1, 1.2343) as the reference material, in this study for the first time the method of an in-situ electrical resistivity measurement was used to measure M_S within a HIP. To investigate the influence of HIP pressure on M_S , resulting microstructures and hardness, specimens were austenitized at a temperature of $T_{AUS} = 1050$ °C for $t_{AUS} = 30$ min at $p_{AUS} = 25, 50, 100$ or 150 MPa. Additionally, the M_S temperature of the same material was determined by quenching dilatometry at ambient pressure for comparison purposes. Characterization of microstructures was conducted by scanning electron microscopy while hardness as an important technological property of tool steels was measured according to the Vickers method. Furthermore, the CALPHAD method was used to compute the thermodynamic influence of pressure on phase stabilities. The experimental results indicate that the method of in-situ resistivity measurement can be used to measure M_S during an integrated HIP heat-treatment process. Besides, a stabilizing effect of pressure on the close packed crystal structure of the austenitic fcc phase is clearly detected, resulting in a reducing influence on the M_S temperature of AISI H11 by up to 90 K.

Keywords: hot-isostatic pressing; martensite start temperature; integrated HIP heat-treatment; electrical resistivity; tools steels

1. Introduction

Hot isostatic pressing (HIP), in general, is a well-known and versatile thermo-mechanical process, primarily applied to high-performance materials. Its key features consist of thermal treatment, usually in a temperature range between RT and 1300 °C (Mo furnace)/2000 °C (graphite furnace) combined with a hydrostatic pressure applied by processing gas, usually

argon or nitrogen, up to values of 300 MPa. Technical applications of HIP range from the densification of engineering ceramics over the closing of pores and shrinkage cavities in as-cast metallic parts to the production of semi-finished products of inert gas atomized metallic powders [1–3].

The latter can be applied to almost every metallic system as long as gas-tight encapsulation and an exceeding of the materials flow stress at HIP temperature can be ensured. Another application gaining more and more importance is the post-processing of additively manufactured (AM) parts [4,5]. In this context, the particular advantage of HIP stems from its ability to close inner defects, such as gas pores, shrinkage cavities and lack of fusion porosity. In this manner, static and cyclic mechanical properties and sometimes corrosion resistance especially of metallic AM parts are improved [6].

Up to now, the influence of the gas pressure within the HIP unit on phase equilibria, phase transformations and precipitation kinetics was of no importance from a technological point of view as the cooling cycle of a standard HIP unit is a rather slow process taking several hours. Thus, all metallic materials gaining their usage properties by sophisticated heat treatment, e.g., Ni-base superalloys or high-alloy tool steels, usually claim for separate post-processing in a precisely controllable thermal process after densification by HIP [7]. Recent advances in HIP technology are aiming at integrating these time and cost intensive post-processing steps directly into the HIP cycle: “integrated HIP heat treatment” is a convenient term for this novel technology [7–11]. As soon as quenching is accessible in a HIP, the influence of pressure on phase stabilities and solid state transformation is gaining major importance [12]. High pressure experimental data on those measures is usually provided in diamond anvil cells up to very high pressure, however, being far away from sample volumes of technical relevance. For these reasons, there is a lack of scientific knowledge on how pressure within a HIP unit influences solid state transformations during a quenching performed within the system [13]. The benefits of such integrated processes result from less processing time, no need for a separate heat treatment device and—as a major concern for sustainable development—less energy consumption compared to a multi-stage process [10,14,15]. Particularly for tool steels, beneficial as well as detrimental effects resulting from integrated HIP heat-treatment can be anticipated: Retarding effects on diffusion controlled formation of soft phases would result in a beneficial increase of hardenability. In contrast, stabilization of the fcc phase against a diffusionless transformation to martensite may result in higher amounts of undesirable and soft retained austenite [16–18].

Thus, the aim of this work is to introduce a method to investigate phase transformations within a commercial laboratory HIP unit equipped with uniform rapid quenching (URQ) technology. The focus is on electrical resistivity measurements as a means to track and quantify the martensitic transformation of a hot working tool steel as it is hardened under pressure inside a laboratory scale sized HIP equipped with a gas quenching unit. Considering safety restrictions and the prohibition of modifications of the pressure vessel, existing feed-through for thermocouples is used to install a four-point electrical resistivity measurement system. It is applied to a hot working tool steels AISI H11 used as a model material. In this way, the influence of pressure on the transformation of metastable austenite to α' -martensite is experimentally accessible.

2. Experimental

The HIP system used in this investigation is the deciding factor of how to set up an electrical resistivity measurement system. Thus, the system is described first followed by the actual set up including materials and sample geometry, test parameters and determination of M_s . For the purpose of comparison, the same material but with a modified sample geometry was heat treated in a quenching dilatometer to determine a precise reference value of M_s at ambient pressure. To discuss the influence of pressure on microstructure and micromechanical properties, thermodynamic equilibrium calculations, scanning electron microscopy and micro hardness testing were conducted.

2.1. ERM Inside the HIP

Within the scope of the study, the HIP type QIH9 (Quintus Technologies AB, Västerås, Sweden) with uniform rapid quenching technology (URQ[®]) was used [12]. The QIH9-HIP consists of a pre-stressed and water-cooled wire-wound pressure vessel. It is separated from the cylindrical furnace chamber by a heat shield (Figure 1a). Argon gas is used as a pressure medium for this study. For accelerated cooling after or during heat treatment inside the HIP, the Ar gas is pumped through an inlet nozzle positioned at the bottom of the furnace. The heat shield surrounding the cylindrical furnace chamber allows gas circulation between the water-cooled vessel and the furnace, a compartment containing ceramic spheroids. These ceramic spheroids act as heat sinks and rapidly absorb the heat from the cooling gas. In this way, quenching rates comparable to oil quenching can be attained.

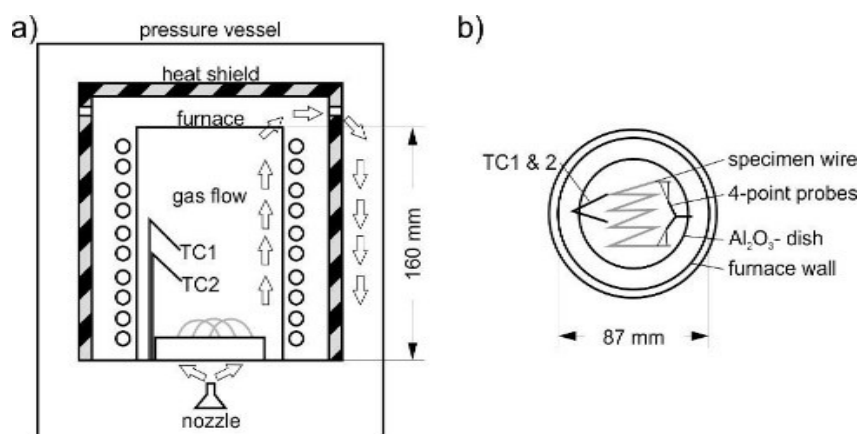


Figure 1. Schematic illustration of the experimental set-up inside the HIP-unit (a) side view, (b) top-view.

In order to determine M_5 a set-up for electrical resistivity measurements (ERM) according to the four-probe method was incorporated inside the HIP furnace. Since the installation of measuring systems in the pressure vessel of the HIP system is limited by safety constraints, the resistance measurement was realized via two wire feed-throughs, which were originally intended for additional thermocouples. Two thermocouples (TC 1 & 2, Figure 1a,b) remain to monitor and control the temperature inside the furnace. The average value of both thermocouples is considered to control the heating power and temperature.

One major challenge of the experimental setup is to detect small changes in electrical resistivity in the course of a rapid quenching process. According to the dependence of resistivity on sample geometry (Equation (1)), the optimal geometry regarding cross section to length ratio is wire material. Its specific resistivity ρ is dependent on the length l , the cross-sectional area A and the resistivity R .

$$R = \rho \cdot A^{-1} \cdot l \quad (1)$$

Therefore, a steel wire of a length of 300 mm and 1 mm in diameter was used as the sample material, even though this geometry is not typical for a hot working tool steel. The steel wire was coiled up loosely to fit into the furnace providing an inner diameter of only 70 mm. The sample was placed inside an Al₂O₃ dish of 60 mm in diameter in order to electrically insulate the specimen material from the HIP furnace and prevent it from short-circuiting. In accordance with the four-probe method, Pt6Rh wires were spot welded to the specimen at four spots being 10 mm apart from each other at both ends of the sample wire (Figure 1b). The measuring current was kept constant at $I_{meas} = 500$ mA using an external power source. The corresponding voltage was measured as a function of time by a Nano Volt/Micro Ohm Meter (type 34420A, Keysight Technologies, Keysight Technologies).

Deutschland GmbH, Böblingen, Germany) and logged with a rate of 1 s^{-1} using BenchVue Digital Multimeter Pro Software (version 3.1, Keysight Technologies Deutschland GmbH, Böblingen, Germany). The specific resistivity of the material was calculated from the measured voltage according to Equation (2).

$$\rho = U \cdot I^{-1} \cdot A \cdot L^{-1} \quad (2)$$

Here, U is the measured voltage and I the measuring current while A and L describe the wire geometry cross section area and measuring length, respectively. The experimental results of ρ were normalized to the specific resistivity ρ_0 at the beginning of each experiment. Synchronizing the internal measurement of temperature within the HIP over time, the dependence of resistivity on temperature is determined. Finally, the tangent method is applied to ρ/ρ_0 -T-plots in order to determine M_S .

2.2. Dilatometry

In order to evaluate M_S at ambient pressure, a Bähr DIL 805 A/D (TA instruments, former Bähr-Thermoanalyse GmbH, Hüllhorst, Germany) horizontal quenching dilatometer was used. Hollow fused silica rods with a diameter of 4 mm were used as a measurement system. The experimental setup requires samples with a length of 10 mm and an outer diameter of 4 mm, thus, the wire material used for HIP experiments could not be directly measured in the quenching dilatometer. Instead, specimen material was cut into a section of 10 mm in length and tied into bundles with Molybdenum wire (99.95% purity, 0.3 mm in diameter). The bundles consist of twelve sections assembled to a cylindrical shape of approx. 4 mm diameter (Figure 2). In this way, exactly the same material could be used in the HIP and the dilatometer, respectively. Experiments were conducted under a static Helium gas atmosphere after evacuating to $4.0 \cdot 10^{-5}$ mbar. The temperature was controlled using a thermocouple type K spot-welded onto one of the sections the specimens were composed of. Thermal cycles were applied to the material according to the heat treatment in the HIP, thus, the only remaining difference is related to the isostatic pressure. M_S was determined from the cooling curve of relative length change over temperature plots similar to the ERM evaluation applying the tangent method.

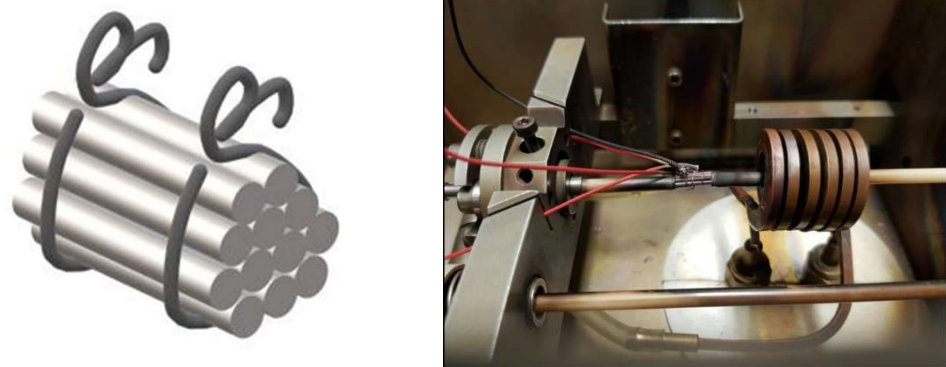


Figure 2. Schematic of specimen wire bundle as used for dilatometry and experimental setup within the quenching dilatometer. One specimen consists of twelve wire sections made of H11 tool steel with an individual diameter of 1 mm and a length of 10 mm. Molybdenum wire with a diameter of 0.3 mm was used to prepare the bundles and minimize thermal and/or chemical influence on the tool steel.

2.3. Material and Heat Treatment

In this study, the ERM method was evaluated using the hot working tool steel H11 (X37CrMoV5-1, 1.2343) as reference material. Specimens were prepared from welding wire (Schweisstechnik Kenn GmbH, Elze, Germany) with a diameter of 1 mm. The welding wire supplied is Cu-plated for enhanced welding processability. This Cu plating was manually

removed by grinding with SiC grinding paper of 1000 mesh to prevent Cu contamination during high temperature processing. The full chemical composition was determined by spark optical emission spectrometry (spark-OES) of 200 g wire material remelted in a melting furnace prior to analysis. The carbon content of the wire was measured via combustion gas analysis (Table 1).

Table 1. Chemical composition of the welding wire made of AISI H11 (X37CrMoV5-1, 1.2343) determined using spark-OES and combustion gas analysis (the latter for C only). All values are given in mass-%.

Material	C	Cr	Mo	Si	V	Mn	Fe
X37CrMoV5-1	0.36	4.75	1.19	1.03	0.42	0.36	Bal.

The HIP heat treatment consisted of heating to an austenitizing temperature at a rate of 15 K/min, solution annealing in the austenite regime at a temperature of 1050 °C for 30 min to dissolve carbides followed by subsequent cooling. In this study, two different types of cooling were employed. For fast cooling, quenching technology with an inlet nozzle of 3.2 mm bore diameter was used (uniform rapid quenching, “URQ”) while for slow cooling heating elements were turned off and no fresh gas was pumped inside the vessel (natural cooling, “NC”). An average temperature of 100 °C was set as the final cooling temperature, after which the heat treatment was completed. Table 2 gives an overview of pressures and cooling variations considered in this study. Detailed characterization was focused on hydrostatic pressures of 25 MPa and 150 MPa to keep the experimental effort in a manageable range. For microstructural analysis, an additional wire piece with a length of 20–30 mm was placed inside the Al₂O₃ dish next to the measuring wire coil in each HIP heat treatment. After heat treatment, transverse sections of these specimens were prepared for further investigation of the microstructure by cutting, hot mounting in conductive resin, grinding with SiC paper and polishing with a diamond suspension to a final polish of 1 µm.

Table 2. Parameter sets of HIP heat treatment. A constant heating rate of 15K/min, a dwell time of 30 min and an austenitizing temperature of 1050 °C were applied, followed by natural cooling or quenching.

Condition	HIP Pressure in MPa	Type of Cooling
1	25	URQ
2	50	URQ
3	100	URQ
4	150	URQ
5	25	NC
6	100	NC
7	150	NC

2.4. CALPHAD Calculations

The influence of pressure on phase stability was calculated utilizing ThermoCalc[®] Software version 2021a and database TCFE10. Property diagrams were obtained for temperature and pressure regimes up to 1500 °C and 500 MPa. The phases considered in the calculation were liquid phase (LIQUID), austenite (FCC_A1 or FCC_A1#2(500 MPa)), ferrite (BCC_A2), MC (FCC_A1#2 or FCC_A1(500 MPa), M7C3 (M7C3_D101) and M23C (M23C6_D84). Martensite start temperatures were calculated according to Barbier [19] for the nominal alloy composition, which represents the composition of austenite at the solution annealing temperature of 1050 °C (Table 1).

2.5. Microstructural Characterization

For microstructural characterization, a MIRA3 FE-SEM was used. To contrast the martensitic microstructure of wire cross sections in secondary electron contrast, polished samples were etched with V2A etchant. Images of varying magnification were taken at

20 kV acceleration voltage and a working distance of 10 mm. Contrast and brightness were digitally optimized for purposes of better comparability in terms of average brightness values performed using ImageJ software (version 1.49 v).

2.6. Hardness Measurements

Hardness measurements with a load of 1 kg (HV1) were performed using a fully automated system KB30S (KB Prueftechnik GmbH, Hochdorf-Assenheim, Germany) with a Vickers indenter on polished sample surfaces. These measurements were performed to find out whether quenching under a hydrostatic gas pressure leads to a stabilization of retained austenite in H11 tool steel, accompanied by a softening effect in the as-quenched state. To compare mean hardness values, HIP wire samples were tested with five indents placed on the wire cross section at least 200 μm apart from each other and from the surface of the samples. Embedding of samples with a minimum length of 10 mm in an upright position and measuring on the front surface ensured sufficient material thickness and a reliable measurement. At the hardness achieved, the indentations were at most about 30 μm wide and thus sufficiently far from each other and also from the surfaces of the specimen. Regarding the dilatometer wire bundles, only outer wires were tested to minimize the influence of different cooling conditions compared to inner wires. Mean values and standard deviations were calculated from at least five measurements of each condition.

3. Results and Discussion

To better understand the impact of elevated hydrostatic pressure, the theoretical influence on phase equilibria was investigated by means of thermodynamic equilibrium calculations based on Gibbs free energy minimization. Figure 3a shows the phase quantity diagram of the investigated hot working steel. A closeup of the temperature regime around the $\alpha \rightarrow \gamma$ transformation, being of special interest for the hardening of steels, is illustrated in Figure 3b. The dashed line represents the stability region of the respective phases at a hydrostatic pressure of 500 MPa.

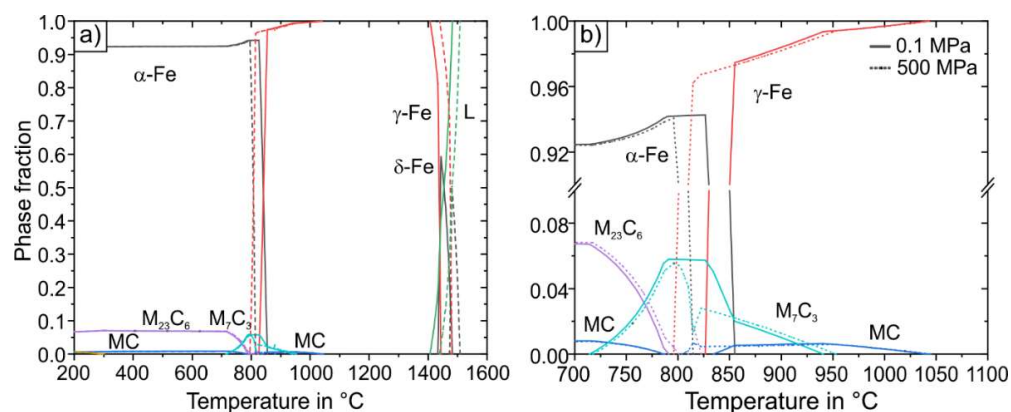


Figure 3. Phase fraction diagram of X37CrMoV5-1 calculated using the CALPHAD method showing (a) the full stability range of all phases and (b) considered carbides in detail.

According to the equilibrium calculation depicted in Figure 3a, the solidification starts with the formation of δ -Fe at 1490 °C and continues with the crystallization of γ -Fe at 1475 °C. The δ -Fe transforms into γ -Fe in a temperature range of 1490–1475 °C. At a solidus temperature T_{sol} of 1475 °C the solidification is completed to a fully austenitic microstructure. A single phase field of the γ -Fe phase is present below T_{sol} down to 980 °C. Below that temperature, 1 vol.-% of V-rich MC carbides is formed from the γ -Fe solid solution. At even lower temperatures, a Cr-rich M_7C_3 -type carbide is stabilized and the MC-type carbide disappears. The γ -Fe $\rightarrow$ α -Fe transformation starts at a temperature below 852 °C and is completed at 827 °C. Meanwhile, due to the lower carbon solubility of the α -Fe phase, the amount of M_7C_3 carbide increases from 2 vol.-% up to 6 vol.-%. At

temperatures below 800 °C, the M_7C_3 -type carbide starts to transform into Cr-rich carbides of type $M_{23}C_6$. Additionally, a V-rich MC carbide is formed at temperatures below 760 °C. Finally, at temperatures below 725 °C, the M_7C_3 carbide disappears and 1 vol.-% of MC and 7 vol.-% of $M_{23}C_6$ carbides are accompanied by an α -ferritic matrix.

Comparing the stability regions of these particular phases in dependence on pressure (0.1 MPa vs. 500 MPa) it can be deduced that T_{sol} and T_{liq} are increased by about 25 K under increased pressure (Figure 3a, dashed lines). Additionally, in the solidification range, the amount of δ -Fe is significantly decreased from 60 to 45 vol.%, although its stable temperature span remains unaffected. Focusing on solid state transformation in Figure 3b, it becomes evident that the γ -Fe $\rightarrow$ α -Fe transformation is shifted to lower temperatures by 20 K and 16 K, respectively. Because of the increase in T_{sol} and the decrease of $T_{\gamma-\alpha}$, the γ -Fe field is widened. At the same time, the equilibrium fraction of carbides remains unaffected by increased hydrostatic pressure, while their temperature range of stability is shifted to lower temperatures in accordance with the shift of $T_{\gamma-\alpha}$. The apparent stabilization of the closely packed γ -Fe phase is in accordance with the theory and observations that the crystal phase with a higher density is favored under increased hydrostatic pressure [13]. Experimentally observed changes in phase transformations are explained by the pressure dependence of the Gibbs free energy.

Figure 4 depicts two exemplary T - p - t -profiles of HIP heat treatments of two different cooling modes. The integrated heat treatment inside the HIP unit starts with the evacuation of the pressure vessel followed by pre-pressurization up to 20 MPa while the temperature is kept constant at 50 °C. Hereafter, the heating process is initiated with a rate of 15 K/min. During heating, the processing gas expands, accompanied by a continuous increase of hydrostatic pressure. Simultaneously, additional fresh gas is pumped into the vessel to help reach the final pressure level for the hardening stage. The average temperature level remains at 1050 ± 1 °C after reaching holding temperature and pressure. At the subsequent cooling step, approximately 70% of that pressure is maintained. This is achieved by introducing fresh cool gas to the vessel through the bottom nozzle as fast cooling is initiated. At that moment, the set value of final pressure for heat treatment is briefly exceeded. The cool gas absorbs heat, flows from bottom to top inside the furnace chamber, passes the heat shield, cools off and descends to the water-cooled pressure vessel wall. More process gas is injected until the final cooling temperature is reached. This compensates to some extent for the pressure decrease resulting from temperature dependent gas relaxation. Finally, the process is completed after dumping the remaining gas from the vessel, during which the furnace is kept at 100–150 °C for several minutes to prevent the freezing of gas pipes (not included in Figure 4). The average cooling times ($t_{8/5}$) depending on cooling mode and process pressure are summarized in Table 3.

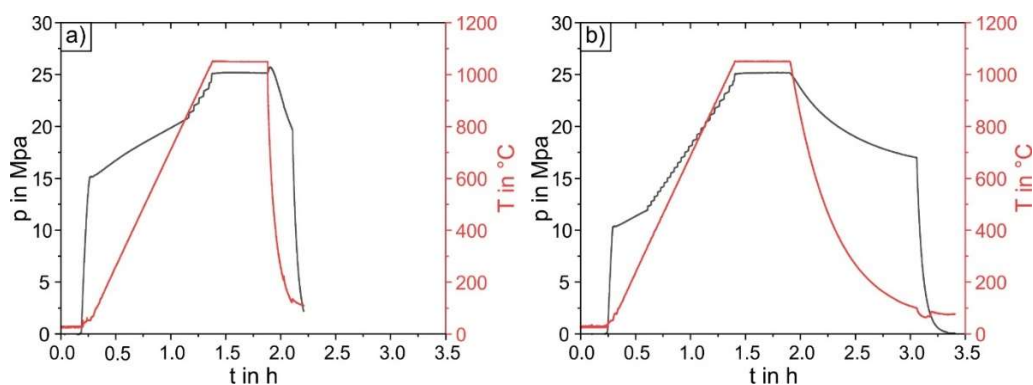


Figure 4. Exemplary p - T - t diagram of a HIP cycle at $p = 25$ MPa for the two cooling modes (a) URQ and (b) NC highlighting how pressure is build up within each section of the heat treatment.

Table 3. Phase transformation temperatures as calculated using ThermoCalc software (pressure dependent calculations) as well as experimentally determined by means of dilatometry (DIL, ambient pressure) and electrical resistivity measurements (ERM, hydrostatic pressure) for varying cooling rates and pressures.

HIP Cycle	CALPHAD		DIL		M_s	ERM		M_s	DIL/ERM $t_{8/5}$ in S
	$T_{\alpha-\gamma}$ start	$T_{\alpha-\gamma}$ finish	$T_{\alpha-\gamma}$ start	$T_{\alpha-\gamma}$ finish		$T_{\alpha-\gamma}$ start	$T_{\alpha-\gamma}$ finish		
NC 25	824	853			347 ± 35	847	890	292	719
NC 100	820	847			–	851 ± 4	900 ± 6	315	424
NC 150	817	843			352 ± 7	841	894	298	407
URQ 25	824	853	825 ± 11	915 ± 24	290 ± 10	–	–	269	138
URQ 50	–	–			341 ± 41	–	–	249	62
URQ 100	820	847			–	–	–	247	51
URQ 150	817	843			316 ± 13	–	–	249	51

High process pressures result in distinctly faster cooling. Doubling the hydrostatic pressure from 25 to 50 MPa reduces the cooling time evaluated between 800 °C and 500 °C by 55% to one minute. This effect is not as pronounced for higher process pressures. Increasing the pressure from 50 to 100 MPa results in a reduction of cooling time by 18% and no further reduction at 150 MPa. Similarly, cooling without introducing fresh cool gas (NC) takes about 12 min at a set pressure of 25 MPa compared to 6 min 47 s at 150 MPa, which is another 17 s faster than at 100 MPa.

To experimentally investigate the pressure influence on phase transformations inside the HIP, critical cooling rates for martensite formation need to be achieved. In Figure 5a mean cooling rates as measured in the process gas are depicted. They depend on the cooling mode and hydrostatic pressure utilized for the respective heat treatment. As illustrated in a schematic CCT diagram of AISI H11 (Figure 5b), the cooling rates employed in this study allow for fully martensitic microstructures to develop. Under the slower continuous cooling conditions provided by NC, a more distinct formation of proeutectoid carbides can be expected while proeutectoid ferrite and pearlite are not expected to be present in the microstructures. Thus, the HIP cycles applied on AISI H11 within this study are expected to reveal only austenite to martensite transformations. Experimental evidence focusing on the four different URQ states is provided in Figure 6. A few undissolved carbides, visible as light spots within the martensitic matrix within the SEM micrograph (Figure 6d), remain after 30 min at 1050 °C, but were too small to be analyzed via EDS and thus not further considered within this study. Significant differences between the three fast cooled martensitic states are not visible by SEM investigation as a direct consequence of the similar cooling rates for pressures of 50, 100, and 150 MPa. In contrast, the microstructure obtained after quenching inside the HIP unit with a pressure of 25 MPa reveals a decoration of grain boundaries visible on the left-hand side of Figure 6a.

Figure 7 shows the results of Vickers hardness measurements (HV1) in dependence on the isostatic pressure within the HIP unit. For a given HIP pressure, the results are differentiated by URQ and NC cooling mode. Additionally, hardness values of samples treated at ambient pressure within the quenching dilatometer are provided for the purpose of comparison. The time-temperatures cycles within the dilatometer were precisely adjusted to the ones within the HIP unit to be able to unveil solely the influence of pressure. All hardness values are within a range of 650 to 715 HV1, depending on the parameter set used for quenching. A clear correlation between process pressure and hardness cannot be deduced, even though it can be anticipated from a theoretical point of view [13,20]. A higher process pressure is accompanied by (a) faster cooling and (b) a lowered M_s temperature (Table 3). Thus, the probability of stabilizing retained austenite and a corresponding softening effect in the as-quenched state is increasing. A rudimental tendency of lower hardness with increasing pressure can be interpreted in the results, at least for the URQ

states (HIP URQ). However, as the dilatometric results (cf. DIL “URQ”) are closely reflecting the same trend, it is expected to depend rather on cooling rate than on hydrostatic pressure.

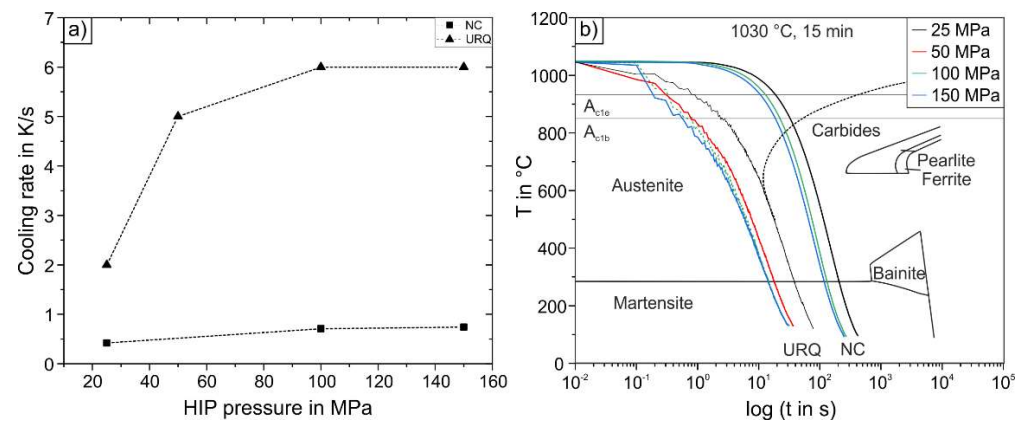


Figure 5. (a) Cooling rates achieved inside the HIP unit for different cooling modes (URQ and NC) and pressures and (b) cooling curves added to a schematic continuous cooling transformation (CCT) diagram.

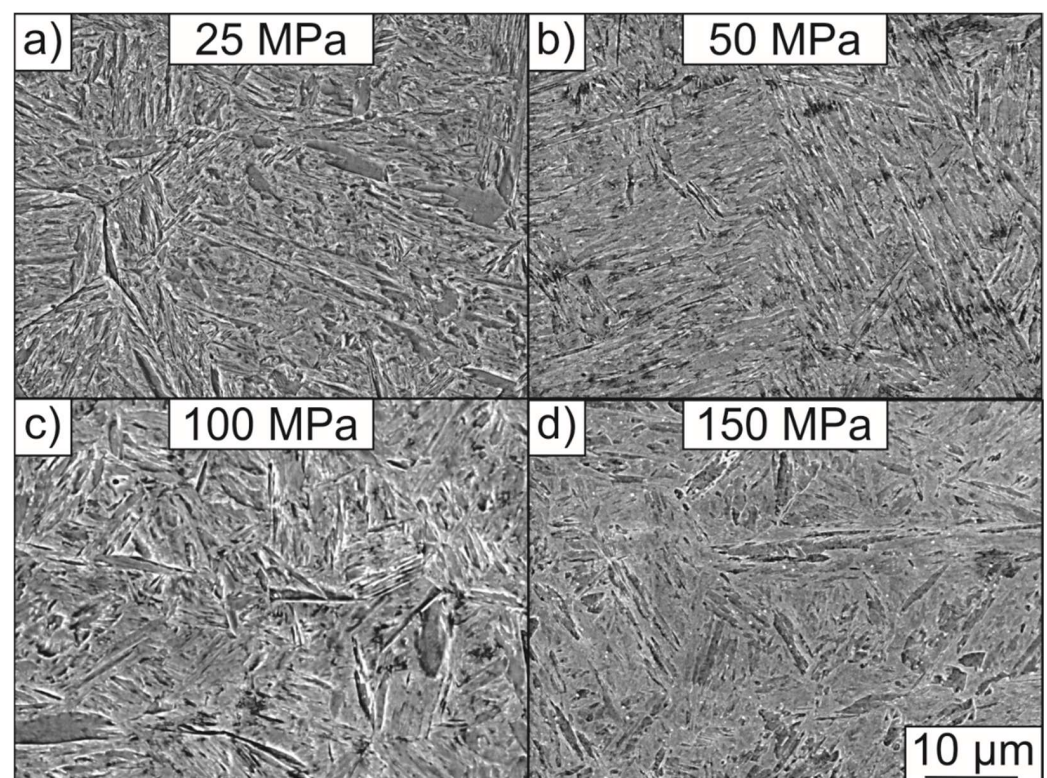


Figure 6. Martensitic microstructure after integrated HIP heat treatment of X37CrMoV5-1 wire material resulting from different processing pressures and corresponding cooling rates in quenching mode (URQ).

As a means to give evidence of the pressure influence on phase transformation, the method of four-point measurement of specific electric resistivity ρ was incorporated inside the HIP unit. In this way changes in ρ were measured in the course of an integrated HIP heat treatment. Phase transformations within an URQ-HIPa show the results obtained for AISI H11 in a ρ/ρ_0 - T plot of the HIP heat treatment NC150 (150 MPa, natural cooling). During heating with a rate of 15 K/min to 1050 °C, resistivity increases as expected with increasing temperature. The increase is almost linear at temperatures below 400 °C and

departs from linearity to higher temperatures. Between 700 °C and 800 °C, an inflection point can be noticed followed by a decreasing relative resistivity around 850 °C (point A in Figure 8a). After passing through a temperature interval of approximately 50 K (point B in Figure 8a), an increasing linear trend in resistivity is measured. For the holding time of 30 min at 1050 °C, the resistivity remains constant. Upon cooling ($t_{8/5} = 407$) resistivity decreases again in an almost linear manner without noticeable inflection points. At an average temperature of about 300 °C (point C in Figure 8a), relative resistivity changes again abruptly followed by a transformation interval of about 100 K prior to passing over into a linear decrease with temperature again. It has to be mentioned, that the heat treatment cycle within the HIP unit was repeated several times without a change of the wire sample for the sake of experimental effort. In this respect, the black line in Figure 8a shows the initial curve of the soft-annealed AISI H11 wire material while the red curve is exemplarily shown for one of the consecutive cycles. Differences are clearly visible in the first section of the initial curve while the transformation expected at point C remains unaffected by the number of cycles.

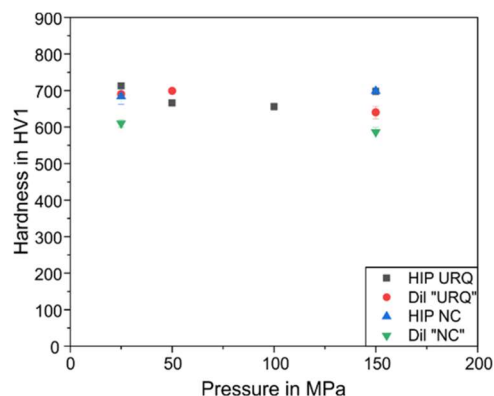


Figure 7. Results of hardness tests (HV1) of X37CrMoV5-1 wire material heat treated under different process pressures and corresponding cooling rates inside a HIP. For comparison, hardness values of wire bundles similarly heat treated in a quenching dilatometer under ambient pressure are denominated as (DIL “URQ”) and (DIL “NC”).

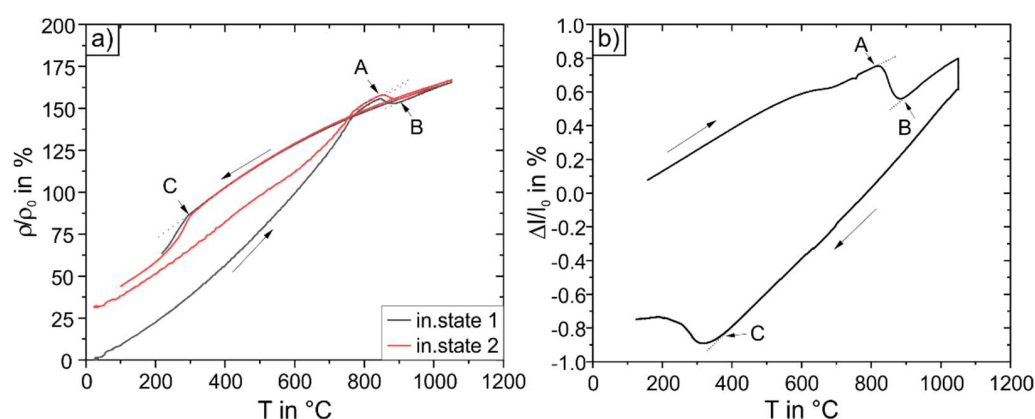


Figure 8. Results of the heat treatment NC150 (a) under hydrostatic pressure inside the HIP based on the ERM and (b) under ambient pressure using dilatometry.

For comparison, the dilatometry result of a bundle specimen (cf. Figure 2) subjected to the same T - t profile of heat treatment NC150 but under ambient pressure is depicted in Figure 8b. The relative length of the bundle specimen increases linearly with temperature during heating to 500 °C followed by an inflection point and a further increase up to about 830 °C (point A in Figure 8b). After passing a temperature interval of about 50 K, a linear

increase of the relative length change is measured (point B in Figure 8b). Dwell at 1050 °C is accompanied by an isothermal contraction followed by a linear decrease upon cooling. At point C the signal deviates from linearity and passes through a comparatively broad transformation temperature range. Linearity of the dl/l_0 signal to lower temperatures can only be presumed.

Applying the results of the aforementioned method in the transformation temperatures listed in Table 3; the points A and B within Figure 8a/b are interpreted as the beginning and the end of the bcc-fcc-transformation, respectively. Point C in Figure 8a/b is of particular interest in the context of this study, as it represents the martensitic transformation of the metastable austenite during cooling. Concerning the dl/l signal, the close packed fcc crystal structure is, as expected, expanded in the course of the martensitic transformation to α' . The relative electrical resistivity, however, is decreased as a consequence of the martensite formation (Figure 8a). The latter result is in accordance with the impact of a γ to α' transformation on thermal conductivity (λ_{th}), a measure primarily determined by the electronic contribution to λ_{th} in most metals and alloys. As Wilzer et al. could show experimentally for a Fe-Ni system, the martensitic transformation starting from a fully austenitic to a partially martensitic microstructure is accompanied by a decrease in thermal resistivity [21].

Focusing on the martensite start temperature measured in this work, several main results can be drawn from the experimental data. First, a close correlation between HIP pressure on the resulting cooling rate (cf. $t_{8/5}$ in s, Table 3) is evident. Up to higher pressure in URQ mode the cooling rate is approaching a saturation level, particularly with respect to 100 MPa and 150 MPa. The latter result is of significant technologic importance as higher pressures are accompanied by higher costs and gas consumption. Taking the CCT diagram (Figure 5b) into account, low cooling rates are associated with a proeutectoid formation of carbides and thus, depletion of the metastable austenitic matrix, particularly from carbon. This effect destabilizes the austenite and is the main reason for increasing M_S values with lowering the cooling rates. On the other hand, a direct comparison of the M_S temperatures determined by dilatometry and resistivity measurements for a given $t_{8/5}$ allows judging the influence of processing pressure. In accordance with the thermodynamic calculations, the close packed fcc phase is stabilized by increasing pressure with a reducing influence on M_S . The decreasing effect on M_S can be quantified to $\Delta T = 40\text{--}50$ K and is thus, expected to be relevant from a technological point of view. The difference is even more distinct considering URQ is under high pressure within the HIP unit, leading to M_S temperatures of about 250 °C only. A steady trend concerning hardness in the as-quenched condition is, however, not visible (Figure 7). Based on these results it can be inferred that stabilization of retained austenite (RA) in the course of a high-pressure heat treatment is not relevant at least for AISI H11, as high amounts of RA would go along with a measurable decrease in hardness [22]. For higher alloyed grades with lower M_S temperatures, e.g., high speed steels, a distinct stabilization of retained austenite by integrated HIP treatment can be anticipated. The experimental verification of this assumption will be a question of future work.

4. Conclusions

Within this work, a method was introduced allowing for the in-situ measurement of phase transformations within a novel hot isostatic press system equipped with uniform rapid quenching technology. It could be shown that electrical resistivity measurements are able to detect the γ to α' martensitic transformation using wire material of AISI H11 as a model alloy for a typical hot working tool steel. A distinct influence of HIP pressure on the M_S temperature could be found experimentally and compared to the transformation temperature at ambient pressure. Potential applications of this technology are expected in the field of the post-processing of additively manufactured metallic materials being dependent on specific heat treatment to obtain their final usage properties. Further applications are expected in energy efficient production processes of near-net-shape parts made of high-alloyed PM materials. The main findings of this work are:

- Phase transformations within a URQ-HIP unit can be measured by electrical resistivity measurements.
- HIP pressure exerts a double influence during integrated HIP heat treatment: First on thermodynamic phase stability and second on the resulting cooling rates being related to the CCT behavior of a specific material.
- The M_s temperature of AISI H11 is reduced by up to 90 K in URQ mode as a consequence of the stabilization of the austenite by pressure.
- A decrease in hardness as a consequence of higher volume fractions of retained austenite could not be measured.
- Integrated HIP heat treatments are considered a comparatively new but promising technological pathway to increase the resource and energy efficiency of high performance materials.

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