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Comparison of densification kinetics of a TiAl powder

by spark plasma sintering and hot pressing

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Abstract

Densification kinetics by spark plasma sintering (SPS) and hot pressing (HP) have been compared, under isothermal conditions and with heating rates of 20°C/min. Careful calibration of sample temperature has been carried out to obtain comparable results. In all cases, densification kinetics did not exhibit significant differences, ruling out any influence of the SPS current. The stress exponent n and the activation energy Q of the Norton law describing deformation at high temperature of the powder particles have been determined by isothermal experiments at different stresses and temperatures, respectively. The values obtained, $n = 1.9 \pm 0.3$ and $Q = 308 \pm 20$ kJ/mol for SPS, $n = 1.5 \pm 0.3$ and $Q = 276 \pm 40$ kJ/mol for HP, come close in both techniques. Using these values, anisothermal densification kinetics at heating rates of 20°C/min and 100°C/min, typical of the SPS, could be analytically reproduced, using literature models. The activation parameters suggest that

1 SPS densification kinetics occurs by dislocation climb controlled by Al bulk diffusion, that is,
2 by classical metallurgical mechanisms.
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5 *Keywords:* spark plasma sintering; hot pressing; plasticity; titanium aluminides.
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8 **1. Introduction**

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10 This study reports on the densification kinetics of a TiAl powder by spark plasma
11 sintering (SPS). This technique consists in uniaxially pressing powders in graphite molds
12 heated by high intensity electric current pulses. This allows very fast heating rates, and thus
13 densification [1] or synthesis [2] cycles lasting typically less than 1 hour, that is, up to 10
14 times less than that of the conventional processing techniques. Many studies have attributed to
15 the electric current pulses an *intrinsic* contribution to the acceleration of the densification,
16 different from the Joule effect, and several phenomena occurring at the necks between the
17 powder particles were invoked. Local overheating by formation of arcs and plasmas between
18 the particles has been postulated [3, 4], and experimentally observed by optical microscopy
19 [5] and by insitu atomic emission spectroscopy [6]. Given these sparking mechanisms, local
20 melting phenomena occurring at the contact zones of powder particles in various materials
21 have been observed [6-8], theoretically analyzed [9] and simulated [10]. Another localized
22 electric effect put forward is that of an intensifying electric current density at the necks
23 between the powder particles, which may cause these zones to melt [11, 12]. Finally, very
24 high current densities at the necks are believed to induce electromigration [13] or
25 electroplasticity [14] phenomena, which are likely to accelerate densification kinetics.
26 However, the above electrically-induced phenomena are still controversial, and assessment of
27 their intrinsic contribution to the densification kinetics remains scarce. In the case of low
28 electrical conductivity materials (eg, Zirconia), densification under isothermal conditions by
29 means of SPS and by a current free technique, the hot pressing (HP), seems to exhibit close
30 kinetics, even if slight differences in mechanisms have been reported [15]. For a material with
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1 a higher electrical conductivity (quasi-crystalline AlCuFeB), densification experiments by
2 means of SPS and HP have been carried out, but with different conditions, making
3 comparisons difficult [16]. It was concluded that the sintering mechanisms were probably
4 close in both techniques. Finally, a recent study has compared HP and SPS kinetics in
5 isothermal and anisothermal conditions, with a highly conducting powder (Cu), and with a
6 calibration of the sample temperature between the two techniques. It was concluded that
7 densification kinetics were identical, and that the SPS current had no intrinsic effect on
8 densification [17].
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20 Here, we investigate the intrinsic effect of the SPS current on the densification kinetics of
21 an intermetallic conducting powder (TiAl, GE composition : $Ti_{48.7}Al_{47.3}Cr_{1.9}Nb_2$) by SPS and
22 HP in isothermal and anisothermal conditions, with calibration of the sample temperature in
23 both techniques. In addition, the macroscopic activation parameters are determined and
24 compared to literature values. Finally, it is shown how the densification kinetics by SPS can
25 be analytically determined, provided the activation parameters are accurately known. These
26 results are important in our opinion, because shaping of TiAl alloys by SPS (for turbine
27 blades applications for instance [18]) will require assessing the densification kinetics in
28 sophisticated molds from the constitutive relations of the alloy at high temperature. Moreover,
29 as the SPS route has shown these materials to exhibit interesting, not to say outstanding
30 mechanical properties [18-23], these alloys are therefore suitable for high temperature
31 applications in aircraft turbine blades or in turbochargers. Thus, the shaping issue will become
32 increasingly important, and will necessitate basic inputs with respect to the densification
33 kinetics.
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53 **2. Experimental**

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55 A spherical gas atomized GE TiAl powder ($Ti_{48.7}Al_{47.3}Cr_{1.9}Nb_2$, Crucible) of
56 granulometry *ca.* 100-150 μm has been employed. Prior to the experiments, the powder has
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been equilibrated at 1200°C for 5 min by SPS, but in a special mold in which no pressure and no electric current was applied to the powder. This allowed equilibration in vacuum of the particle microstructure by transformation of dendritic as-gas atomized metastable α [24] into equilibrium $\gamma + \alpha$ [20, 25] microstructure. The aim of this procedure was to avoid that microstructure changes in the powder activated by temperature would superimpose and interfere to the phenomena activated in the SPS and HP experiments. Consequently, the microstructure of the powder particles consisted in an equilibrium near γ microstructure containing 4% vol. of α_2 phase which did not evolve during densification [26].

For both SPS and HP experiments, graphite molds about 20 mm in inner diameter were employed. However, the other dimensions of the molds were not the same. The molds used for HP, which were typical of this technique, had thicker walls than the molds used for the SPS experiments. The reason was that accidental breaking of the molds could have damaged the heating system of the HP, and had therefore to be absolutely avoided. These molds were not suitable for the SPS experiments, because there was a too high difference between the punch diameter (20 mm) and the outer diameter of the molds (between 65 mm and 73 mm), which would have given strong electric current concentration in the punches, and therefore high thermal gradients in the samples and in the molds. Thus, the dimensions of the SPS and HP molds were as follows:

- SPS molds: inner diameter: 20.8 mm, outer diameter: 40 mm, height: 48 mm.
- HP molds: inner diameter: 20.4 mm, outer diameter: varying from 65 mm to 73 mm, height: 120 mm.

A graphite foil (Papyex) was employed, to ensure sealing and lubrication. Its thickness was 0.4 mm and 0.2 mm for the SPS and HP molds, respectively. Thus, in both cases, the sample diameter was 20 mm. To obtain accurate densification curves, the ratio between final

1 thickness and diameter of the sample had to be as low as possible, to minimize the friction of
2 the powder on the lateral walls of the molds [27]. Then, 3.92 g of the equilibrated powder was
3 introduced in the molds, giving a sample thickness at full density of 3 mm. During the SPS
4 cycle, the molds were surrounded by graphite felt, to limit the thermal gradients in the
5 samples [28].
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11 For the SPS experiments, a Sumitomo 2080 machine has been used. First, the chamber of
12 the SPS was evacuated to ≈ 10 Pa. The uniaxial pressure was set to the desired value (25 MPa
13 to 75 MPa) and applied for one minute. While pressure was applied, the heating cycle was
14 initiated. The samples were then heated to 570°C within 5 min. This was followed by heating
15 at 20°C/min (some experiments were carried out at 100°/min). This heating rate was selected
16 to be the same as in the HP experiments, which is limited to 20°C/min. For the isothermal
17 experiments, this heating was followed by a plateau of 1 h (some experiments have
18 nonetheless been interrupted after 15 min and 30 min) at constant sample temperatures
19 between 865°C and 1075°C. At the end of the cycle, the heating current was stopped and the
20 pressure released. The cooling rate of the molds in the SPS chamber was about 150°C/min.
21 For the anisothermal experiments, heating was maintained at 20°C/min throughout the cycle,
22 until a temperature of $\approx 1300^\circ\text{C}$ was reached. Then, heating was halted. The temperature was
23 measured on the external wall of the molds using an optical pyrometer, beginning at 570°C.
24 The pulse sequence of the SPS current was the common “12-2” type (12 current pulses and 2
25 timeouts). The current was measured by the magneto-electric sensor of the machine, which
26 yields a value close to the average of the time-dependent signal of the current [29]. The
27 current actually flowing through the sample has been estimated to 30 % of the total SPS
28 current, following the study by Misawa *et al.* on metallic materials [30]. Shrinkage of the
29 sample due to densification was measured by the displacement of the lower punch with an
30 accuracy of about ± 0.005 mm.
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2 For the HP experiments, the equipment from the MATEIS laboratory was employed. It
3 consisted of a uniaxial hot press Goliath (Stein Heurtey, Physiterm). The die containing the
4 powder was externally heated with a graphite resistance. The maximum load applied to the
5 punches was 200 kN for a maximum temperature of about 2200°C. Heating took place under
6 vacuum (~10 Pa). Temperature was measured on the surface of the mold using an optical
7 pyrometer (beginning at 250°C) and the temperature cycle was obtained by a W-Rh
8 thermocouple. All the anisothermal experiments were carried out with a heating rate of
9 20°C/min. The uniaxial pressure was set to the desired value identical to the SPS experiments
10 (25 to 75 MPa) and applied in 3 minutes. At the end of a cycle, resistance heating was stopped
11 and pressure released. The cooling rate of the die in the HP chamber was about 20°C/min.
12 Displacement of the upper punch was measured by a wire potentiometer with a precision of
13 about ± 0.01mm.
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29 Because temperatures in the SPS and HP experiments were measured on the external
30 surface of the molds, the sample temperature was not known and had to be determined by
31 calibration. This was performed by melting Al (660°C), Cu (1085°C), and by using the
32 change in TiAl microstructure at the α transus (γ + lamellar below 1335°C, fully lamellar
33 above 1335°C [28]). The onset of melting (see example of Cu melted by SPS in Fig. 1a), and
34 the crossing of the α transus (see an example in HP experiment in Fig. 1b-c), could be
35 determined within about ± 10°C and ± 12.5°C, respectively. The calibration curves thus
36 obtained, yielding the sample temperature T_{sample} as a function of the temperature given by the
37 pyrometer T_{pyro} , are plotted in Fig. 2.
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52 Quantitative determination of the relative density $D(t) = \rho(t)/\rho_{\text{th}}$, with $\rho(t)$: density of the
53 sample at time t , and ρ_{th} : theoretical density of the sample at full density (= 3.95 g/cm³ for
54 TiAl), during the SPS and HP cycles were performed using the following expressions, which
55 can be easily derived:
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$$D(t) = D_f \frac{e_f}{e_f + d_f - d(t)} \quad (1)$$

$$D_f = \frac{\rho_f}{\rho_{th}} \quad (2)$$

$$\rho_f = \frac{m}{v_f} = \frac{m}{\pi \frac{\phi^2}{4} e_f} \quad (3)$$

With D_f : final relative density of the sample, e_f : final thickness of the sample, $d(t)$ and d_f : position at time t and final position of the mobile punch of the SPS and HP, ρ_f final density, m : mass of the sample, v_f : final volume of the sample, and ϕ : diameter of the sample (=20 mm). In the densification curve, the value of the final relative density of the sample D_f is denoted using a symbol. It has been geometrically determined by measuring e_f , ϕ and m and by using Eqs (2) and (3). To remove the contribution of the deformation of the graphite tools (elastic deformation due to applied pressure and thermal dilatation), punch displacement has been recorded in the conditions of the densification experiments, but without sample (blank test). Then, $d(t) = d_p(t) - d_b(t)$, with $d_p(t)$: un-corrected punch displacement in the densification experiments, and $d_b(t)$: punch displacement in the blank tests.

3. Results

The aim of this study was to compare the densification kinetics obtained by SPS and HP. Densification experiments in isothermal (at different temperatures and applied loads) and anisothermal conditions have then been performed with both techniques.

3.1. Isothermal conditions

3.1.1. Densification cycles

Fig. 3a-b shows temperature (measured by pyrometer) and pressure profiles during SPS and HP densification cycles. Both profiles are very much alike, except for the temperature

1 reading which begins at 570°C and 250°C in the SPS and HP experiments, respectively. This
2 does not impact the results, because up to about 800°C, no densification occurs in TiAl [26].
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4 Another difference is a larger contribution of the deformation of the graphite tools, d_b , by HP
5 than by SPS (Fig. 3a-b). This is due to the larger size of the HP molds. Finally, the current
6 density flowing through the sample J and the voltage U tend to exhibit constant values during
7 the isothermal plateau of the SPS experiments (Fig. 3c). These values increase with plateau
8 temperature: J and U go from 57 A/cm² to 74 A/cm², and from 1.68 V to 2.14 V, when
9 temperature increases from $T_{\text{sample}} = 865^\circ\text{C}$ to $T_{\text{sample}} = 1075^\circ\text{C}$, respectively.
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20 3.1.2. Densification curves

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22 To draw densification curves, the isothermal parts (from $t = 0$) of the SPS and HP cycles
23 have been selected, and D has been calculated using Eqs. (1), (2) and (3). Figs. 4 and 5 give
24 isothermal SPS and HP densification curves obtained for sample temperatures between 865°C
25 and 1075°C, and for applied pressures between 33 MPa and 75 MPa. In one case
26 ($T_{\text{sample}} = 969^\circ\text{C}$, $P = 50$ MPa, Fig. 4c), the experiments have been repeated, and geometric
27 measurements of the relative density after experiments interrupted at $t = 0.25$ h and $t = 0.5$ h
28 (shown in Fig. 4c by symbols), have been carried out. These results show that the accuracy of
29 the absolute value of D is about ± 0.02 . The striking feature of these results is that the
30 densification kinetics by SPS and HP are close, the differences being of the order of the data
31 scattering.
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47 3.2. Anisothermal conditions

48 3.2.1. Densification cycle

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50 Fig. 6a shows the time dependence of the parameters during SPS and HP cycles with
51 identical heating rates of 20°C/min. It can be seen that the profiles of sample temperatures
52 (corrected from pyrometer measurement using calibration curves shown in Fig. 2) in the SPS
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1 and HP experiments present reasonably similar evolutions. The dwell pressure is reached
2 within ≈ 2 min by SPS and 10 min by HP, but this difference has no influence of the results,
3 because significant densification occurs only after 10 min (Fig. 6b). In the SPS experiments,
4 the current density in the sample and voltage at the final temperature ($T_{\text{sample}} = 1343^{\circ}\text{C}$) are
5 112 A/cm² (Fig. 6a) and 3.44 V (not shown), respectively.
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12 3.2.2. Densification curves

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15 SPS and HP densification curves obtained in the aforementioned conditions are shown in
16 Fig. 6b. Considering that the experiments have been conducted in two different laboratories
17 using different graphite tools geometries, it can be inferred that both curves are reasonably
18 similar. Hence, the striking feature is that the densification kinetics by SPS is not much faster
19 than by HP.
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28 4. Analysis of the results

29 4.1. Determination of stress exponent and activation energy

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32 By using the isothermal densification curves at different applied stresses, and different
33 temperatures, it is possible to determine the stress exponent n and the activation energy Q ,
34 respectively, assuming that densification occurs by power-law creep. In this case, the
35 deformation rate $\dot{\epsilon}$ of the material making up the powder particles under a stress σ follows a
36 Norton law:
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$$48 \quad \dot{\epsilon} = A_0 \exp\left(-\frac{Q}{RT}\right) \sigma^n, \quad (4)$$

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52 with A_0 : material constant. Then, the densification rate \dot{D} follows the relations given below,
53 provided the contributions of capillary forces and gas trapped in the pores on the effective
54 pressure are disregarded [31, 32]:
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$$\dot{D} = G_1(D)\dot{\epsilon} \quad (5)$$

$$\sigma = G_2(D)P \quad (6)$$

with, for $D < 0.9$:

$$G_1(D) = 5,3(D^2D_0)^{1/3} \frac{1}{\sqrt{3}} \left(\frac{D - D_0}{1 - D_0} \right)^{1/2} \quad (7)$$

$$G_2(D) = \frac{1}{3} \times \frac{1 - D_0}{D^2(D - D_0)} \quad (8)$$

and, for $D > 0.9$:

$$G_1(D) = \frac{3}{2} \times \frac{D(1 - D)}{[1 - (1 - D)^{1/n}]^n} \quad (9)$$

$$G_2(D) = \frac{3}{2n} \quad (10)$$

with: P : applied macroscopic pressure, and D_0 : green density. To describe the mechanical behavior of the powder particles, equivalent (Von Mises) deformation rate $\dot{\epsilon}$ and stress σ are considered. Then, for a given value of D , the plot $\ln \dot{D} = f(\ln \sigma)$ for different values of P at constant T yields a straight line for slope n , and the plot $\ln \dot{D} = f\left(\frac{1}{T}\right)$ for different temperatures at constant P gives a straight line for slope $\left(-\frac{Q}{R}\right)$. These calculations require to determine the densification rate, \dot{D} . This has been performed by adjusting the densification curves $D(t)$ by polynomials, which were then analytically derived with respect to time. For each densification curve, polynomials of different orders, typically between 3 and 6 were attempted, and the solution best fitting the data was selected. Fig. 5b shows two examples of densification curves adjusted by 6th order polynomials. These adjustments had to be carried

1 out with care, because the results were highly sensitive to them. Most of the time, adjustments
2 were not made for the whole densification duration (1 hour), but only at intervals around the
3 values of D selected for the calculations, for a higher accuracy.
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7 In order to calculate n and Q from equations (4) to (10), it is necessary to make the
8 calculations for identical values of D , while keeping unchanged values of geometrical factors
9 $G_1(D)$ and $G_2(D)$ when changing the applied pressure or temperature. In other words, to
10 achieve identical arrangements of powder particles under each pressure and temperature
11 conditions, and to make calculations independent of the geometrical models describing these
12 arrangements. Thus, Fig. 7a shows \dot{D} evolution for D around 0.82, for applied pressures
13 between 25 MPa and 75 MPa. Fig. 7b shows the plot $\ln \dot{D} - \ln P$ for $D = 0.82$, from which n
14 can be calculated. Similarly, \dot{D} has been evaluated around $D = 0.75$ between 865°C and
15 969°C (plot not shown), and the plot $\ln \dot{D} - \ln 1/T$ has been drawn (Fig. 8), from which Q
16 can be obtained. These procedures have been performed with the SPS and HP data. The
17 results are summarized in Table 1. As can be seen, the values obtained by SPS and HP are
18 close. This can readily be accounted for by the similarity of the densification kinetics yielded
19 by these two techniques.
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40 With respect to the determination of n , another method, based on the variation of the
41 effective pressure on the powder particles with variation of D (Eqs. 6, 8 and 10), had
42 previously been developed [15, 16, 27]. Compared with this approach, our procedure presents
43 the advantage of being independent of the model describing the geometry and the mutual
44 indentation of the powder particles, because the G_1 and G_2 functions are constant at a given D
45 value (Eq. (7)-(10)).
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55 *4.2. Analytical calculation of densification curves for different heating rates*

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2 From the activation parameters determined with the SPS isothermal densification curves
3 (Table 1), theoretical anisothermal curves have been calculated and compared with
4 experiments. For this purpose, by numerically integrating over time Eq. 5 with the use of
5 relations (4) and (6)-(10), and by taking for D_0 the experimental green density ($D_0 \approx 0.61$ -
6 0.63), densification curves for 20°C/min and 100°C/min heating rates have been calculated.
7 To do this, the value of A_0 of Eq. (4) had to be adjusted and thus, the activation parameters
8 determined for the SPS isothermal densification, $n = 1.9$ and $Q = 308$ kJ/mol, have been
9 employed. The value of A_0 has been adjusted to fit the experimental densification curve for
10 20°C/min and $D < 0.9$ (Fig. 9a). This gave: $A_0 = 2 \times 10^{-6} \text{ s}^{-1} \text{ Pa}^{-n}$. Then, A_0 and n have been kept
11 constant, and the other curves (20°C/min – $D > 0.9$, 100°C/min – $D < 0.9$ and 100°C/min –
12 $D > 0.9$, Figs. 9a-b), have been computed, by slightly re-adjusting Q to replicate the data. As
13 can be seen, both portions of the curves ($D < 0.9$ and $D > 0.9$) for the two heating rates
14 (20°C/min and 100°C/min) are accurately reproduced, for Q varying within the narrow
15 interval 300-315 kJ/mol. This shows that the densification kinetics in a wide range of heating
16 rates, typical of the SPS experiments, can be reproduced, provided the activation parameters
17 are accurately known.

38 39 **5. Discussion**

40 41 42 *5.1. SPS and HP densification kinetics: influence of SPS current*

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45 The first aim of this study was to compare the densification kinetics by SPS and by HP,
46 under identical conditions in terms of sample temperature, heating rate and applied pressure,
47 to decouple the influence of the SPS current on the densification kinetics from the influence
48 of these parameters. Thus, particular care has been taken to achieve identical sample
49 temperatures in both techniques, by calibrating the measured temperature on the melting
50 points of Al and Cu, and on the α transus of TiAl (Fig. 2). In these conditions, the
51 densification kinetics by SPS and by HP come very close to each other, in isothermal as well
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1 as in anisothermal experiments (Figs. 4-6). In other words, the electric current flowing
2 through the samples, which is $\approx 50-100 \text{ A/cm}^2$, does not accelerate significantly the
3 densification kinetics. The microscopic densification mechanism identified in a previous
4 study is plastic deformation of the powder particles kinetically controlled by dislocation climb
5 involving Al bulk diffusion [26]. Therefore, the electric current of the SPS has no detectable
6 influence on these elementary mechanisms. This is contradiction with the studies which
7 assume an impact of the SPS current on diffusion [13] or on plasticity [14]. However, this is
8 in agreement with a previous study, which showed the absence of effect of strong electric
9 current (higher than 1000 A/cm^2) on the diffusion kinetics in the Ag-Zn system [33]. This is
10 probably due to the fact that very high current densities (of the order of 10^6 A/cm^2) are needed
11 to exhibit significant “intrinsic” effects (other than Joule effect) on diffusion [34]. Then, the
12 typical current density flowing through samples in SPS experiments ($\approx 50-100 \text{ A/cm}^2$) is
13 probably not sufficient to accelerate the elementary mechanisms of plasticity and diffusion
14 involved in densification.
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33 34 5.2. Stress exponent and activation energy 35 36

37 The values of stress exponent and activation energy (Table 1) can be compared with
38 literature values obtained for near γ TiAl alloys, whose chemistry and microstructure come
39 close to the alloy of this study, and tested in similar conditions of temperature and
40 deformation rate (Table 2). As can be seen, the scattering of the results is very broad. Among
41 these studies, some yield $\dot{\epsilon} - \sigma$ curves. They are reported in Figs. 10a and b which also plot
42 deformation kinetics calculated with the activation parameters of the SPS and HP
43 experiments: $Q = 308 \text{ kJ/mol}$, $n = 1.9$, $A_0 = 2 \times 10^{-6} \text{ s}^{-1} \text{ Pa}^{-n}$ for SPS, $Q = 276 \text{ kJ/mol}$, $n = 1.5$, A_0
44 $= 1.5 \times 10^{-4} \text{ s}^{-1} \text{ Pa}^{-n}$ for HP (in the case of HP, the value of A_0 furnishing the best agreement
45 with the literature data has been retained). Clearly, our results lie within the cloud of data
46 found in the literature, which extends, for given temperature, $\dot{\epsilon}$ and σ conditions, over up to
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1 one order of magnitude. This spreading probably originates from a very high sensitivity of the
2 activation parameters on the alloy chemistry and microstructure. Also, it seems that with the
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4 data from the HP experiments (Fig. 10b), the agreement is somehow less satisfactory than
5
6 with the SPS experiment data (Fig. 10a). This is due to the curve slopes, that is, to the n
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8 values. It is then likely that the best value of n is around 2, and that the value obtained with
9
10 the HP experiments ($n = 1.5 \pm 0.3$) is slightly underestimated.
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14 The values of activation parameters n and Q give a hint at the densification mechanisms,
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16 following the sintering theories [35, 36]. The low value of n , around 2, suggests that kinetics
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18 is controlled by diffusion. Moreover, the activation energy measured, 300 kJ/mol, is not far
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20 from the value for diffusion of Al in TiAl, 360 kJ/mol [37]. Diffusion of Al then appears as a
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22 probable mechanism for densification. Microstructural characterizations showed that
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24 densification of TiAl by SPS occurs by deformation at the necks between the powder particles
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26 [20, 26]. This could result from different mechanisms: dislocation glide and climb, volume
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28 diffusion (Nabarro-Herring mechanism), grain boundary diffusion (Coble mechanism) and
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30 grain boundary sliding. Accurate TEM observations evidenced twinning, glide and climb
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32 mechanisms in the neck regions, the kinetics being probably controlled by glide and twinning
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34 in the high effective stress – low temperature regime of the beginning of densification, then
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36 by climb in the low effective stress – high temperature regime of the end of densification [26].
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38 The analyses of this study suggest that, by being part of the dislocation climb, Al diffusion
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40 controls the densification during most of the SPS cycle, dislocation glide and twinning being
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42 active only at the very beginning of the cycle, when the contact areas between the powder
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44 particles are almost restricted to points, leading to very high local stress. In summary, both the
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46 macroscopic and microscopic studies point to a dislocation climb controlled by Al diffusion
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48 as the mechanism controlling the densification kinetics during the SPS and HP experiments.
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59 *5.3. Theoretical calculation of densification curves*

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In this study, the apparent activation parameters n and Q have been determined in isothermal experiments (Figs. 7, 8), and used to compute the theoretical anisothermal densification curves at 20°C/min and 100°C/min (Fig. 9). It can be seen in Fig. 9 that, once A_0 is adjusted, the anisothermal densification curves can be accurately calculated, with only a minor adjustment of the value of Q . This shows, in an alternative way, that the densification mechanisms, under a fast heating rate of the SPS, involve classical metallurgical mechanisms. Consequently, the rapidity of the SPS reflects the high heating rate of the powder, without intrinsic current effect.

The determination of the A_0 , n and Q parameters of the powder provides a valuable method for estimating the densification kinetics by SPS. This method could probably be implemented with a high degree of accuracy to estimate the densification kinetics of more complex parts, providing the related temperature, stress and strain fields could be described by appropriate models. However, it can be seen from Fig. 9 that, because the value of the activation energy greatly impacts the densification kinetics, its value has to be very accurately determined.

6. Conclusions

To evaluate the role of the SPS current ($\approx 50\text{-}100\text{ A/cm}^2$) on the densification kinetics, comparisons have been made with the current-free HP technique, with proper calibration of the sample temperature in both cases. Isothermal and anisothermal experiments show that the SPS and HP kinetics exhibit no significant differences. Consequently, the stress exponent (n) and activation energy (Q) are close in both techniques: $n = 1.9 \pm 0.3$ and $Q = 308 \pm 20\text{ kJ/mol}$ for SPS, $n = 1.5 \pm 0.3$ and $Q = 276 \pm 40\text{ kJ/mol}$ for HP. With these data, and with pre-exponential value $A_0 = 2 \times 10^{-6}\text{ s}^{-1}\text{Pa}^{-n}$, anisothermal SPS densification kinetics using typical heating rates (20°C/min and 100°C/min) have been accurately reproduced analytically. These activation parameters are in agreement with those determined in the literature on bulk TiAl

1 samples. They suggest that densification of TiAl by SPS and HP is mostly controlled by Al
2 bulk diffusion, through its involvement in dislocation climb, the mechanisms of dislocation
3 glide and twinning being active only in the small interparticle regions at the very beginning of
4 the densification cycle. In summary, the SPS densification mechanisms involve classical
5 metallurgical mechanisms, without intrinsic contribution of the current.
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11 **Acknowledgements**

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17 have been performed with the Sumitomo 2080 SPS machine of the Plateforme Nationale de
18 Frittage Flash du CNRS (PNF2-CNRS, Paul Sabatier University, Toulouse, France).
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Tables

Table 1. n and Q values obtained.

	HP	SPS
n	1.5 ± 0.3	1.9 ± 0.3
Q (kJ/mol)	276 ± 40	308 ± 20

Table 2. Bibliographic review of the n and Q values.

Alloy	Microstructure	T (°C)	$\dot{\epsilon}$ (s ⁻¹)	n	Q (kJ/mol)	Ref.
Ti ₅₇ Al ₄₃	52% γ +48% α_2	1000-1100	10^{-5} - 10^{-2}	2-4	390	[38]
Ti ₄₈ Al ₄₈ Cr ₂ Nb ₂	γ +10-15% α_2	600-1050 800	10^{-4} - 10^{-1} 10^{-4} - 10^{-3}	1.7-4.2 1.7-2.2	200	[39]
Ti ₄₉ Al ₄₇ Cr ₂ Nb ₁ Ta ₁	50%(γ + α_2)+50%B2	800-1000	10^{-6} - 10^{-4}	2	210	[40, 41]
Ti ₄₈ Al ₄₇ Mn ₂ Nb ₂ B ₁	Near γ			2.6		[42]
Ti _{50.8} Al _{46.8} Cr _{2.2} Mo _{0.2}	Duplex			2.5	345	[43]
Ti ₄₈ Al ₄₈ Cr ₂ Nb ₂	γ + α_2	950-1150	10^{-3} - 10^{-1}	2.8-8	335	[44]
Ti ₅₃ Al ₄₇	γ + α_2	600-900	10^{-8} - 10^{-7}	2.3	340	[38]
Ti ₄₈ Al ₄₈ Cr ₂ Nb ₂	γ +10-15% α_2	750-850	2×10^{-4} 5×10^{-3}	1.7 4	194	[45]
Ti _{50.8} Al _{46.8} Cr _{2.2} Mo _{0.2}	γ + α_2	800-900	2×10^{-5} - 2×10^{-4}	1.7-2.8	220	[46]

Figure captions

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3 Fig. 1. (a) Punch displacement d as a function of pyrometer temperature T_{Pyro} during an
4 experiment of melting of Cu (melting temperature: 1085°C) by SPS. When Cu melts, at
5 $T_{\text{Pyro}} = 1058^{\circ}\text{C}$, the punch displacement accelerates sharply (arrow). TiAl γ + lamellar (b), and
6 fully lamellar (c) microstructures in HP experiments interrupted at pyrometer temperatures of
7 1350°C (b) and 1375°C (c). The pyrometer temperature for α transus is then:
8 $T_{\text{pyro}}(\alpha) = 1362.5 \pm 12.5^{\circ}\text{C}$.
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12 Fig. 2. Calibration curves of sample temperature (T_{sample}) as a function of measured
13 temperature by external pyrometer (T_{pyro}) in SPS and HP experiments, for melting of Al
14 (660°C), Cu (1085°C) and for the TiAl α transus (1335°C).
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18 Fig. 3. Recordings of T_{pyro} , P , d_p and d_b for SPS (a) and HP (b) cycles, in experiments of
19 isothermal densification during 60 min at $T_{\text{sample}} = 969^{\circ}\text{C}$ (corresponding to $T_{\text{pyro}}(\text{SPS}) =$
20 950°C , and $T_{\text{pyro}}(\text{HP}) = 1023^{\circ}\text{C}$). Time origin is taken at the beginning of the isothermal
21 plateau. (c) Recordings of U and I in the case of the SPS experiment, and plot of J ,
22 considering that 30% of the SPS current flows through the sample.
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26 Fig. 4. Isothermal densification curves at different temperatures ($P = 50$ MPa).
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29 Fig. 5. Isothermal densification curves. (a) $P = 33$ MPa. (b) $P = 75$ MPa ($T_{\text{sample}} = 969^{\circ}\text{C}$).
30 Examples of 6th order polynomial fits (see text) are shown as dotted curves.
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33 Fig. 6. (a) P and T_{sample} profiles in the SPS and HP experiments, and J profile (considering
34 that 30% of the current flows through the sample) in the SPS experiments. (b) Densification
35 curves at $20^{\circ}\text{C}/\text{min}$ by SPS and HP.
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38 Fig. 7. Analysis of the isothermal densification curves under different applied stresses
39 ($T_{\text{sample}} = 969^{\circ}\text{C}$). (a) $\dot{D} - D$ curves around $D = 0.82$. (b) $\ln \dot{D} - \ln P$ curves for $D = 0.82$.
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Fig. 8. $\ln(\dot{D}) - 1/T$ plot for \dot{D} evaluated around $D = 0.75$ ($P = 50$ MPa), for T between 865°C and 969°C .

Fig. 9. Analytical calculations of the SPS densification curves, for A_0 adjusted to $2 \times 10^{-6} \text{ s}^{-1} \text{ Pa}^{-n}$, $n = 1.9$ and Q between 300 kJ/mol and 315 kJ/mol . (a) 20°C/min . (b) 100°C/min .

Fig. 10. Norton laws of the TiAl of this study, drawn with the activation parameters determined with the SPS (a) and HP (b) densification experiments. Data available from the literature are also indicated, for comparison purposes.

Fig. 1

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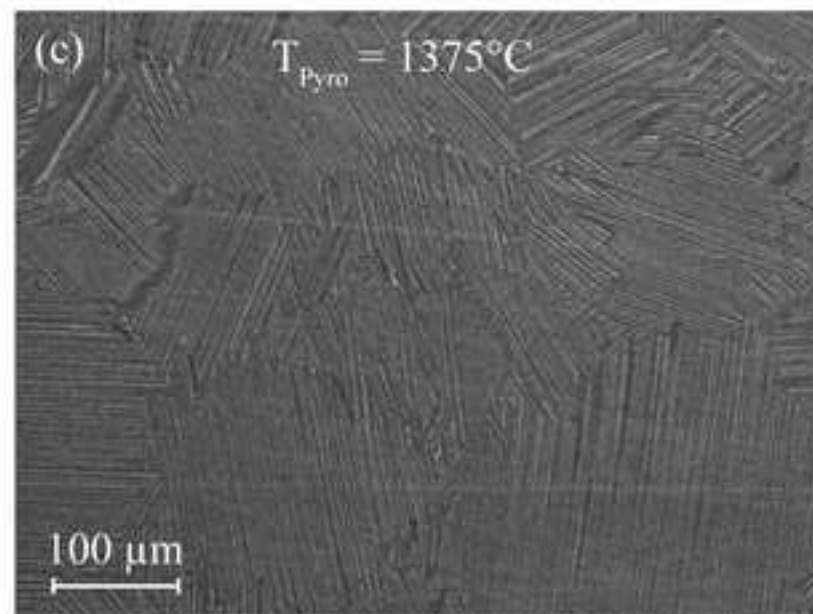
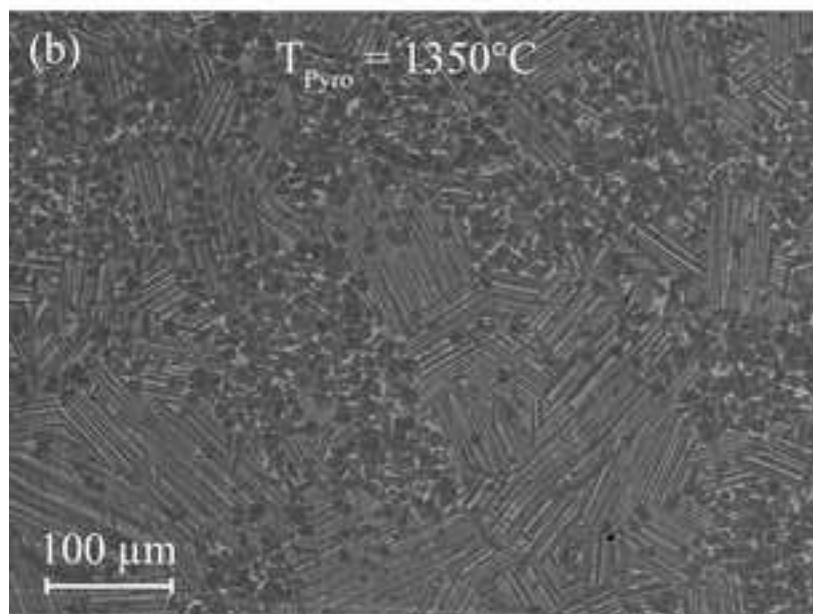
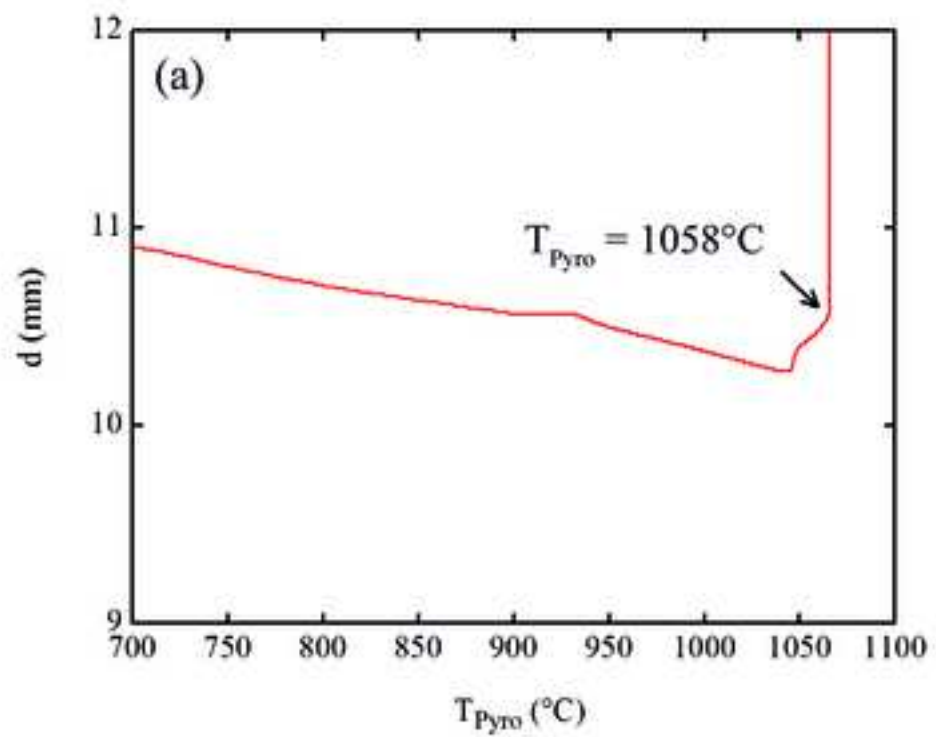


Fig. 2

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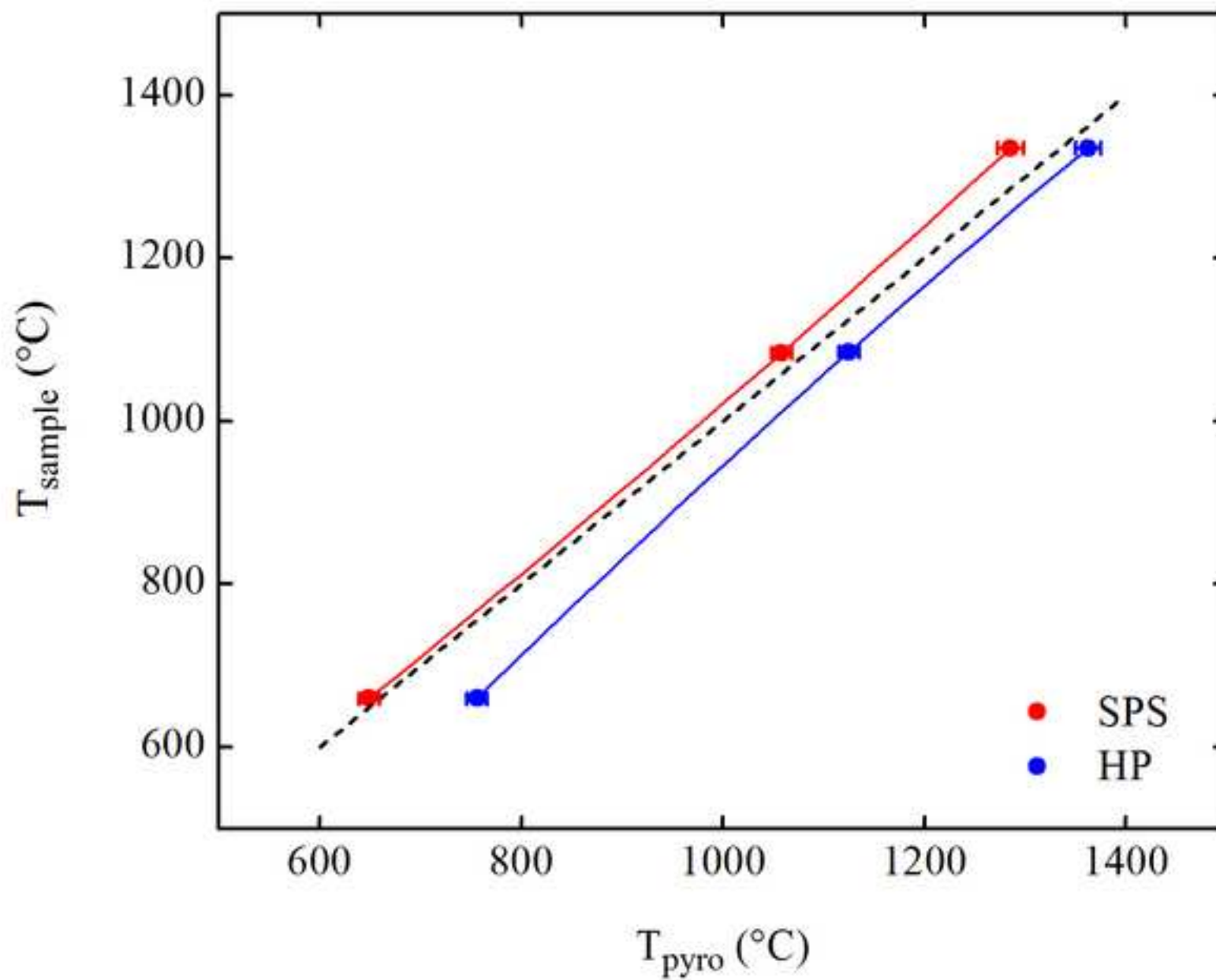


Fig. 3

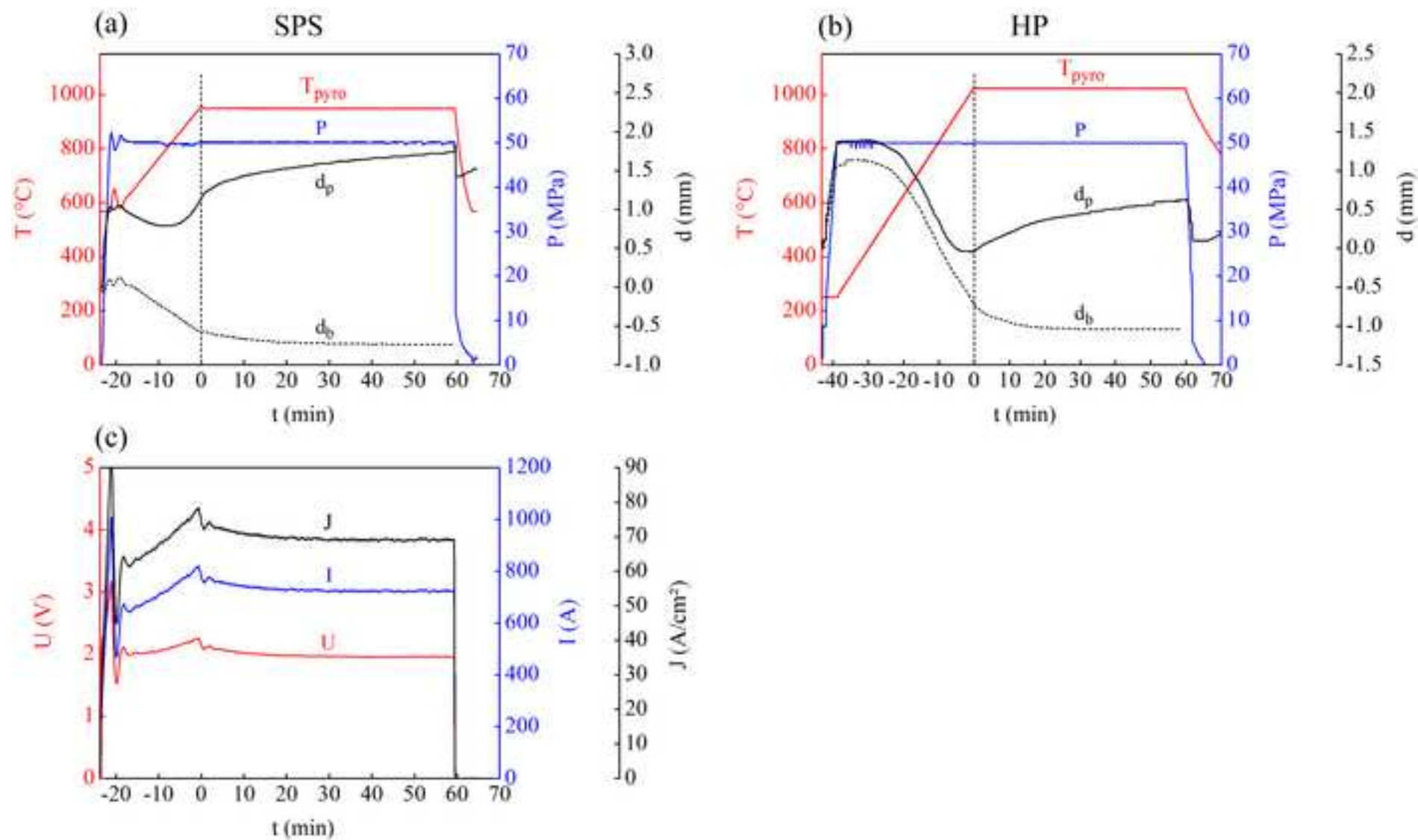
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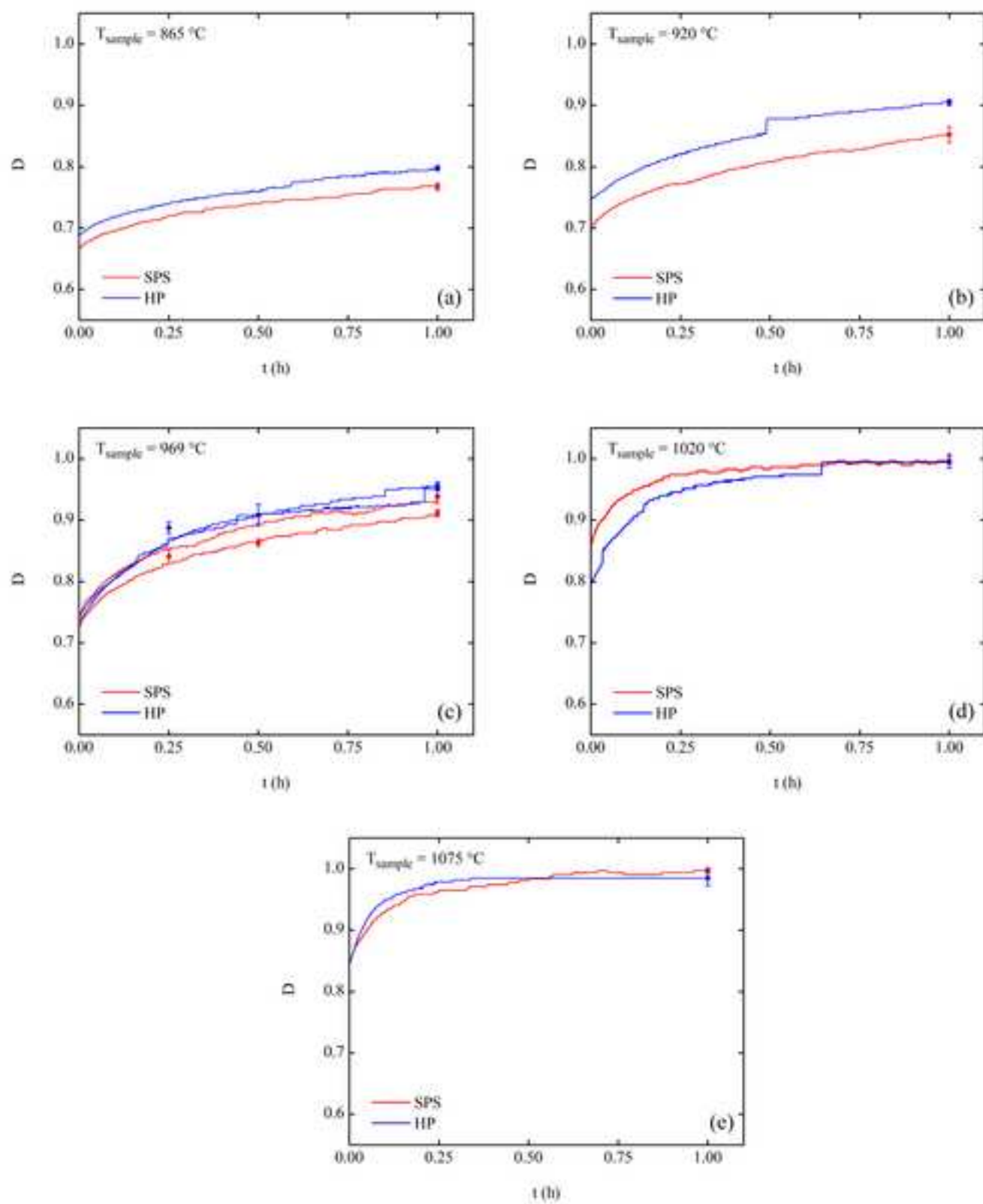
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Fig. 5

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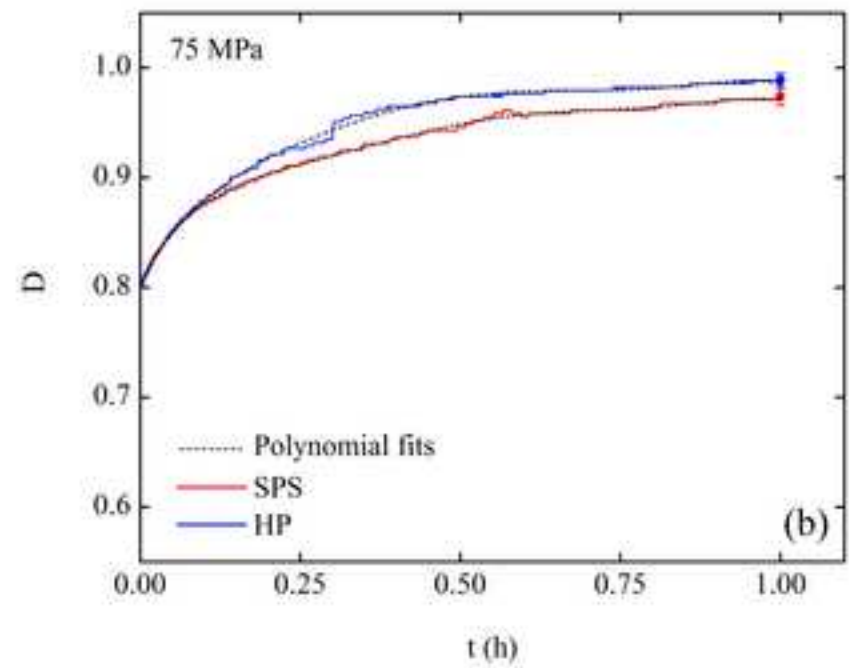
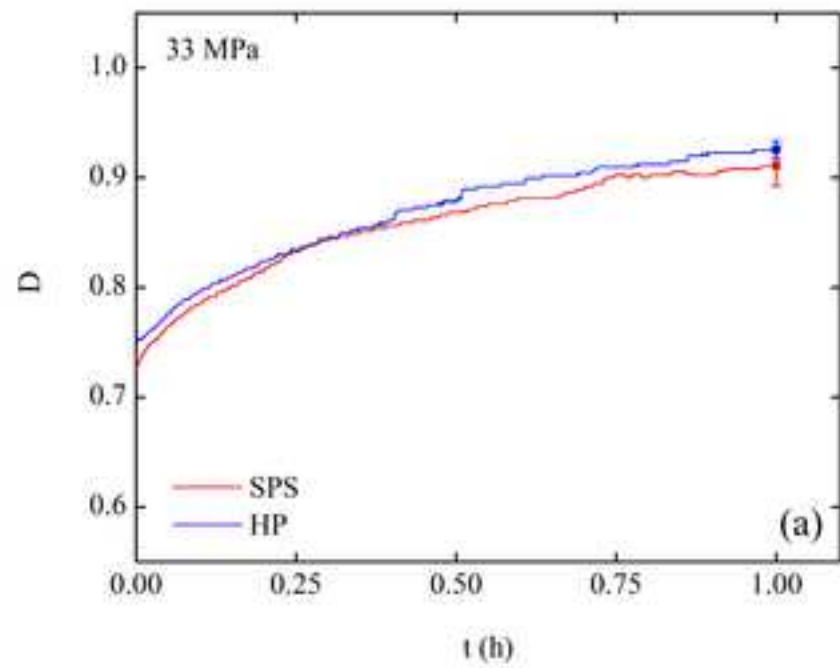


Fig. 6

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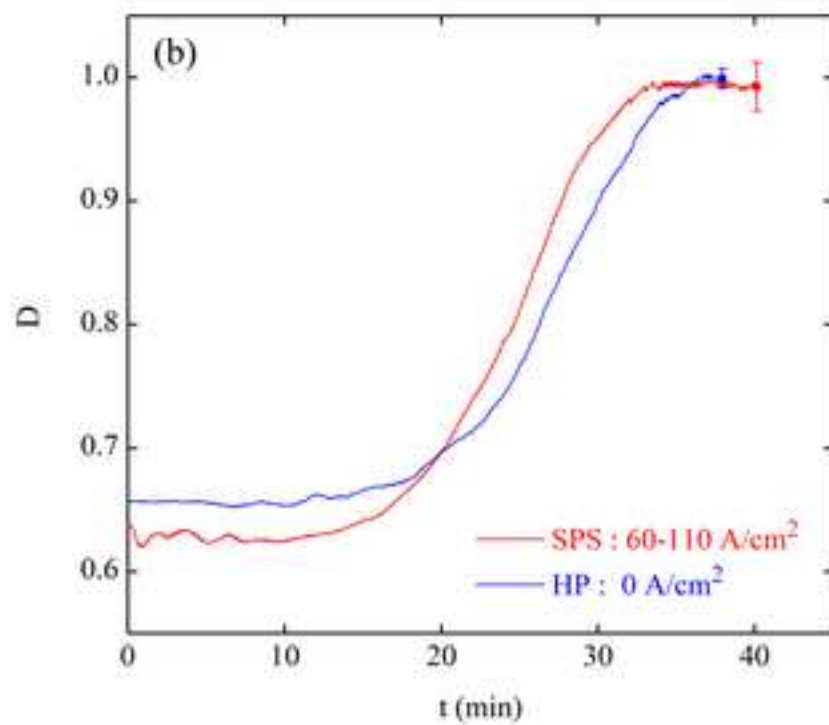
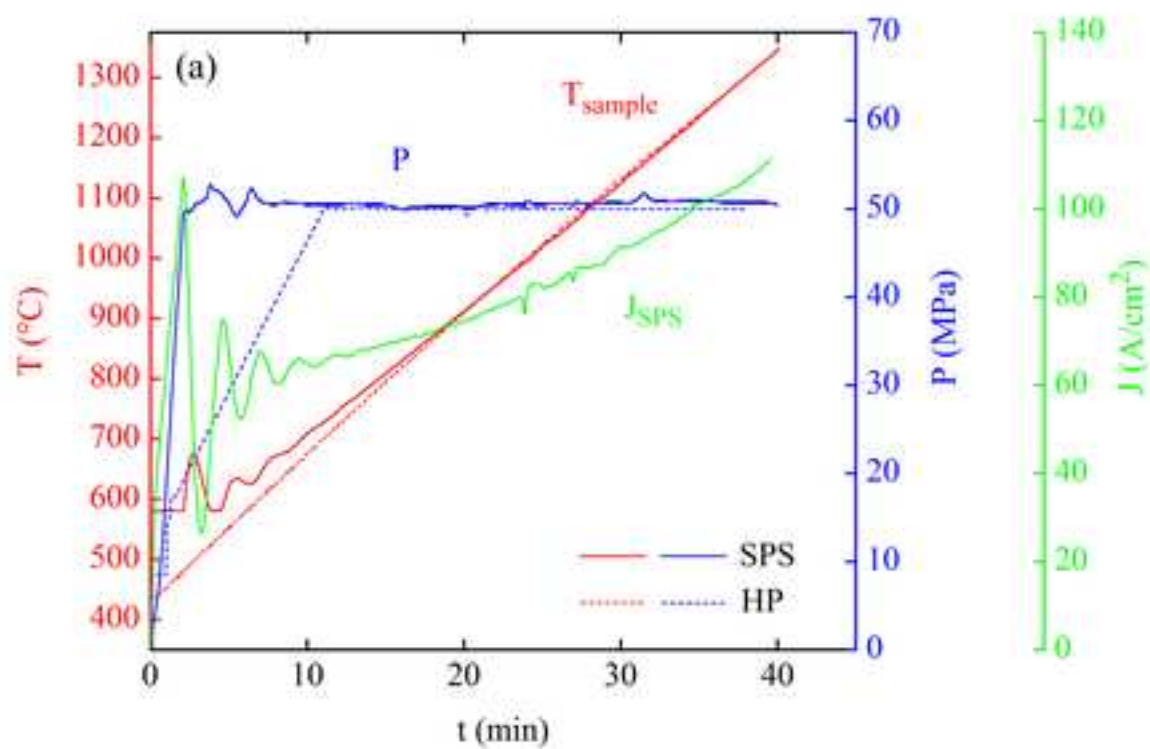


Fig. 7

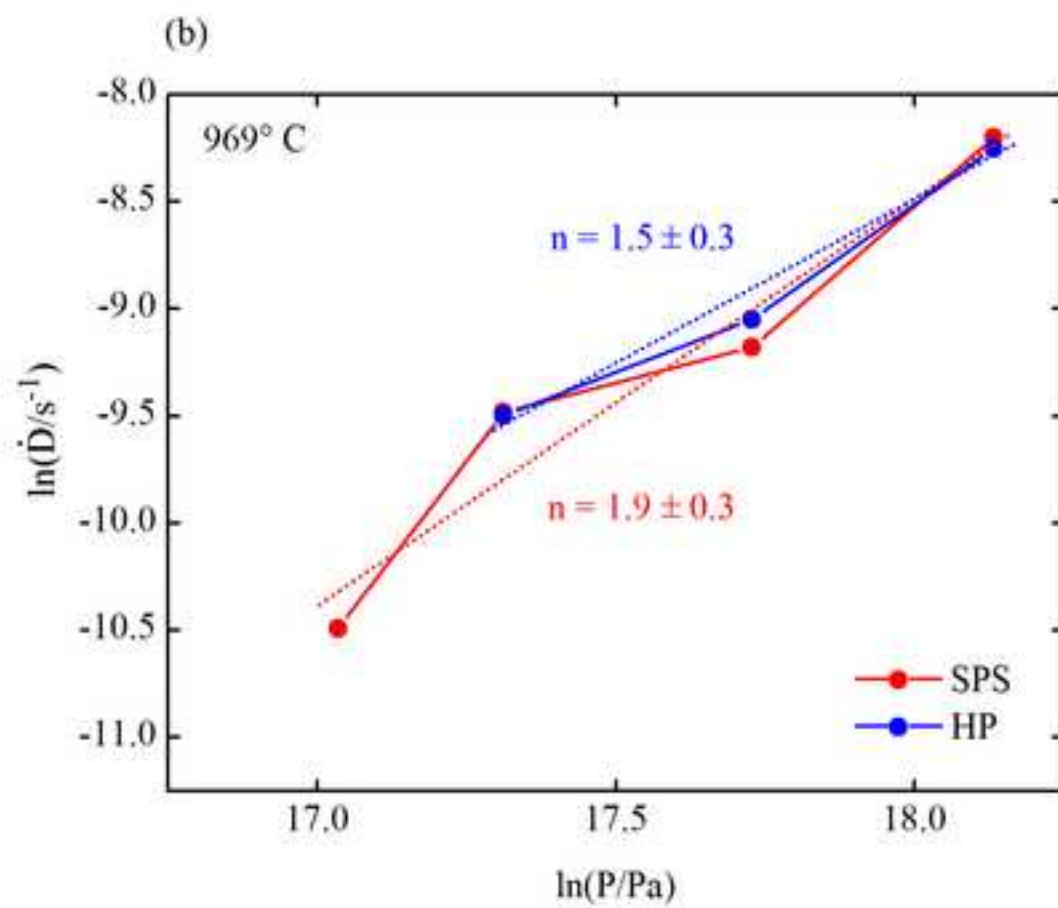
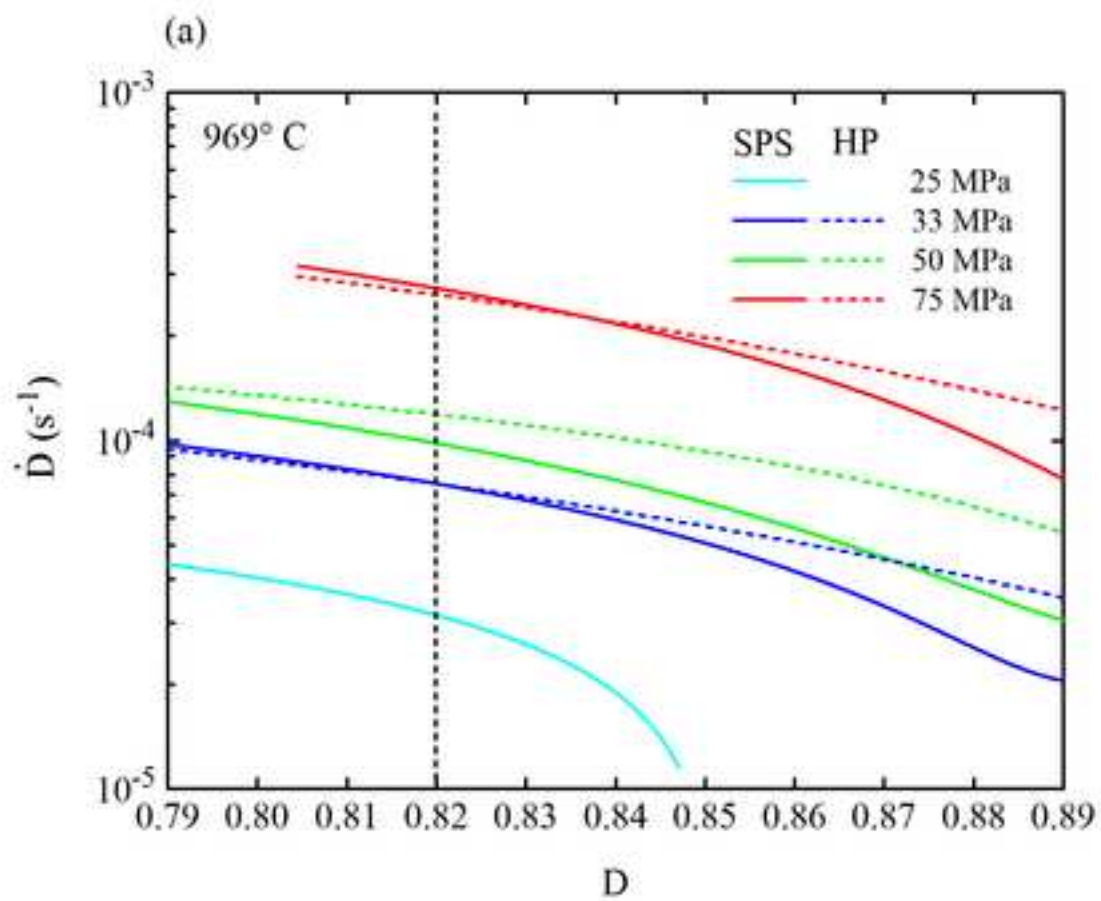
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Fig. 8

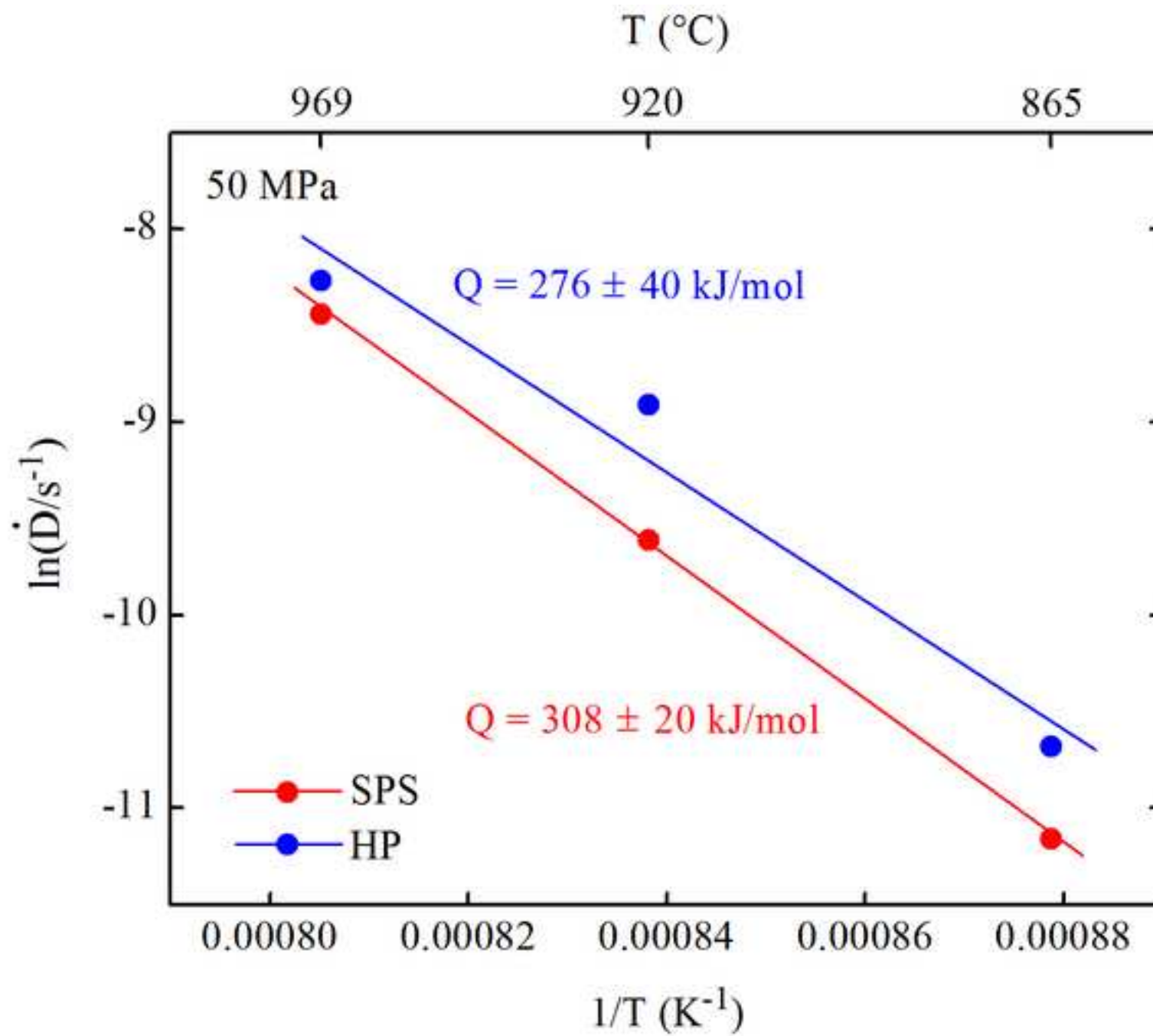
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Fig. 9

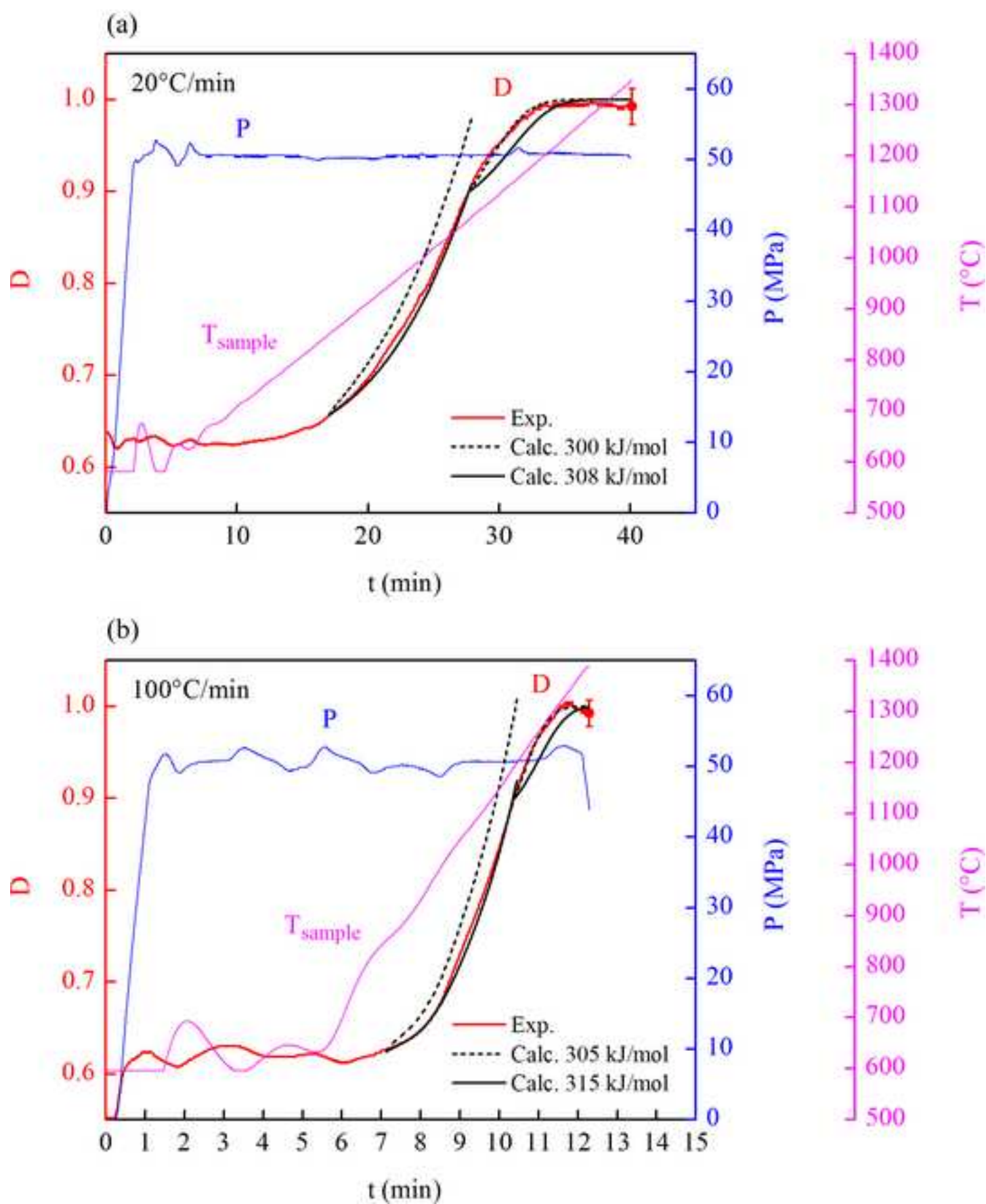
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Fig. 10

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