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DICTRA® SIMULATIONS OF SIGMA PHASE FORMATION IN DUPLEX STAINLESS STEELS

Abstract

In duplex stainless steels (DSS) the desired microstructure after solution heat treatment is a ferritic matrix with austenite islands, maintaining approximately equal amounts of both phases. However, during several manufacturing processes, such as welding, the formation of deleterious phases could happen, and the one of greater influence is the sigma phase, resulting in loss of corrosion resistance and toughness. The present study worked on developing DICTRA® simulation models that could assess the volume fraction of sigma as a function of the aging time of DSS, obtained in previous experimental works of these research team. Simulation models analysed have planar or spherical symmetry with different dimensions for ferrite and austenite. In the models, it was assumed ferrite and austenite volume fractions and compositions as the same obtained in Thermo-Calc® equilibrium calculations of the solution treatment temperature. Sigma phase composition was obtained in equilibrium simulation at the aging temperatures. It was concluded that the simulation model which best assess the formation of sigma phase is a spherical configuration with austenite in the centre, surrounded by ferrite, placing sigma as active phase between the two former phases with negligible thickness.

Keywords

1. Introduction

The combination of high toughness, mechanical strength and corrosion resistance allowed duplex stainless steels (DSS) to be used in oil and gas, chemical, and petrochemical industries. DSS are composed approximately by equal amounts of ferrite (α) and austenite (γ), and high amounts of Cr, Ni, Mo and N. [1, 2]

However, DSS are susceptible to deleterious phase's formation, such as chromium nitrides (Cr_2N), chi (χ) and sigma (σ) [3]. Those phases are usually formed between 823 K (550 °C) and 1273 K (1000 °C) [4-7]. Sigma is the most deleterious phase in DSS, and is mainly formed by Fe, Cr and Mo. Sigma formation is responsible for loss of corrosion resistance due to Cr and Mo depletion of the surrounding matrix [8-10], and occurs preferentially in heterogeneous nucleation sites of the matrix such as α/γ interfaces [11,12,13,14].

Kinetics of sigma phase formation, in a simplified approach, can be described by the Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation [15,16]. Computational modelling of sigma phase is performed by the research group of the authors of this paper [17,18] showing that sigma phase formation kinetics can be also assessed by DICTRA® simulations. Previous paper from one of the authors of this contribution [16] described the kinetics of sigma phase formation during isothermal aging of a UNS S310803 DSS, at temperatures between 700°C and 900°C, presenting experimental data points of sigma phase volume fraction as a function

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of aging time at a specific temperature, and obtaining an adjusted KJMA equation for this phase transformation.

This paper evaluated the possibility of assess the volume fraction of sigma phase formed during isothermal aging through DICTRA® simulations, comparing them to the experimental data found in the previous paper mentioned before [16].

2. Computational modelling

Using Thermo-Calc® version 2018b with TCFE8 database, equilibrium volume fraction of phases and composition of phases were determined for the UNS S310803. It was used the composition of the alloy studied elsewhere [16], Fe-22.2%Cr-5.7%Ni-2.98%Mo-0.16%N, and composition of ferrite and austenite was determined at the temperature were volume fractions of ferrite and austenite were 0.409 and 0.591, the same reported in the reference paper [6]. Equilibrium composition of sigma phase were also determined for the ageing temperatures (700 °C, 750 °C, 800 °C, 850 °C or 900 °C) for use in DICTRA simulations, described in the sequence.

DICTRA® software using TCFE8 database for calculation of local equilibrium at interfaces, and MOBFE3 mobility database to assess diffusion coefficients were used for simulation of the kinetics of sigma phase formation at isothermal ageing temperatures. Two different geometrical models were implemented. The planar model (Fig. 1a) consider uniaxial diffusion perpendicular to the interface between ferrite (α) and austenite (γ), and the length of the phases was set as half of ferrite or austenite mean size of those phase thickness, in accordance to the reference work [16] that indicates phases sizes considering the elongated microstructure of austenite islands in a ferritic matrix. Spherical Model (Fig. 1b) considered a spherical region of austenite with radius equal to the radius of austenite in the reference work [16], surrounded by a volume of ferrite with thickness that generated the volume ratio between ferrite and austenite 0.409:0.591. Sigma was placed in the models as an active phase of negligible size (0.01μm thickness) at α/γ interface. Composition of phases in DICTRA® simulations did not consider N content due to its negligible influence on sigma phase formation, as previously used in literature [18,19]. This procedure avoids N supersaturation problems, and the need in thermodynamic calculations of MN type (Face Centered Cubic, FCC) or M_2N (Hexagonal Close Packed, HCP) nitrides, allowing DICTRA® here proposed.
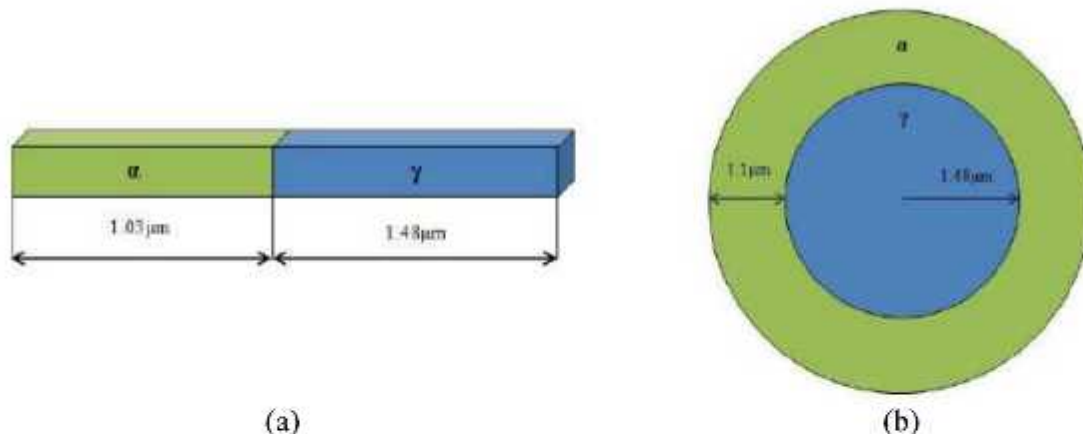

(a)   (b)

Fig. 1. (a) Planar and (b) spherical models used in DICTRA® simulations.

Results of sigma volume fraction from DICTRA® were compared to the experimental results previous published in the reference work [16] already mentioned, in order to validate the models, and by comparison determining which is the best for assessment of the kinetics of sigma phase formation through computational simulation.

3. Results and discussion

Equilibrium volume fractions of phases as a function of temperature are obtained through Thermo-Calc® simulations, and are presented in Fig. 1. The temperature of 993 °C were chosen as the one that allowed volume fractions of ferrite and austenite of 0.409 and 0.591, the same reported in the reference work [16]. Compositions of ferrite and austenite at 993 °C, and compositions of sigma at studied ageing temperatures (700 °C, 750 °C, 800 °C, 850 °C or 900 °C) were determined in Thermo-Calc® and were used in DICTRA® simulations of kinetics of sigma phase formation.
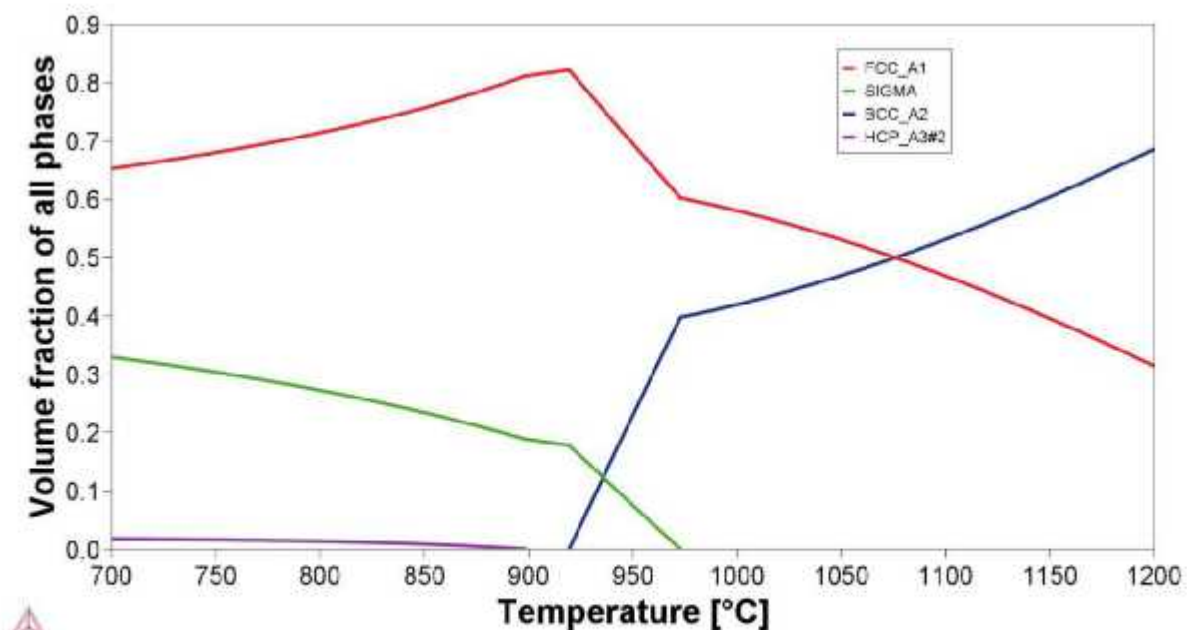

Fig. 2. Equilibrium diagram for the studied steel obtained in Thermo-Calc® simulation with TCFE8 database.

Results of sigma phase volume fraction as a function of isothermal aging times at 700 °C, 750 °C, 800 °C, 850 °C or 900 °C were previously reported by one of the authors [16], and those results were compared to the DICTRA® simulations here proposed, as presented in Fig. 2 to Fig. 6.

As expected, the spherical model simulation results show sigma phase volume fraction growth at higher rates than the planar model, due to the greater number of diffusion flux directions provided by the spherical model, when compared to the planar, where the flow of diffusion is perpendicular to the interface between the phases of the planar model.

The results of the simulations with the spherical model (Fig. 2 to 6) are the ones that better assess the experimental results presented in [16]. However, it should be noted that the proximity of the spherical model simulations to the experimental data is higher at temperatures of 700 and 750 °C (Fig. 2 and 3). This can be an indication that different aging temperatures could lead to changes in sigma formation mechanisms, and the higher the tested temperature, the worst is the assessment of sigma volume fraction by DICTRA® using the

proposed spherical model, which only represents in a simplified manner the complex morphology of sigma phase in aged DSS, as extensively presented in literature [2,13,14,16-19].

4. Conclusions

It was concluded that the simulation model which best assess the formation of sigma phase during isothermal ageing of a UNS S31803 DSS is a spherical configuration with austenite in the centre, surrounded by ferrite, placing sigma as active phase between the two former phases with negligible thickness. However, different aging temperatures could lead to changes in sigma formation mechanisms, and the higher the tested temperature, the worst is the assessment of sigma volume fraction by DICTRA® using the proposed spherical model.
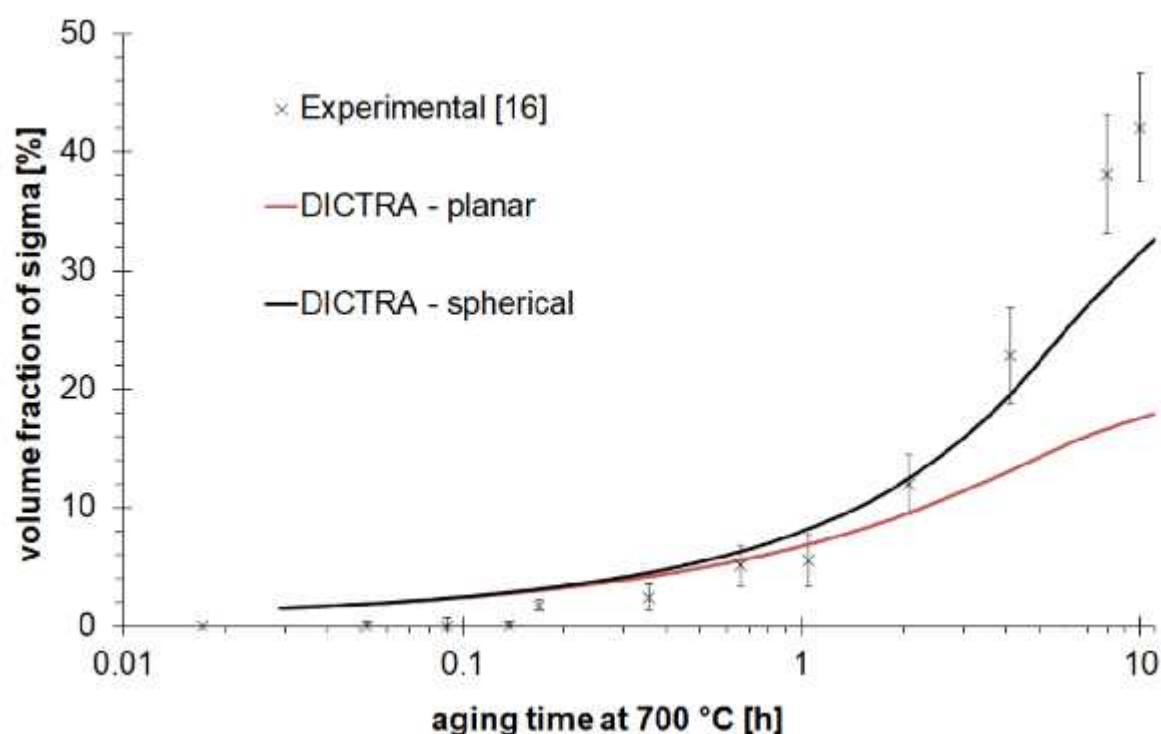

Fig. 3. Volume fraction of sigma as a function of aging time at 700 °C obtained in DICTRA® simulations using both geometrical models proposed in this investigation, compared to experimental results from [16].

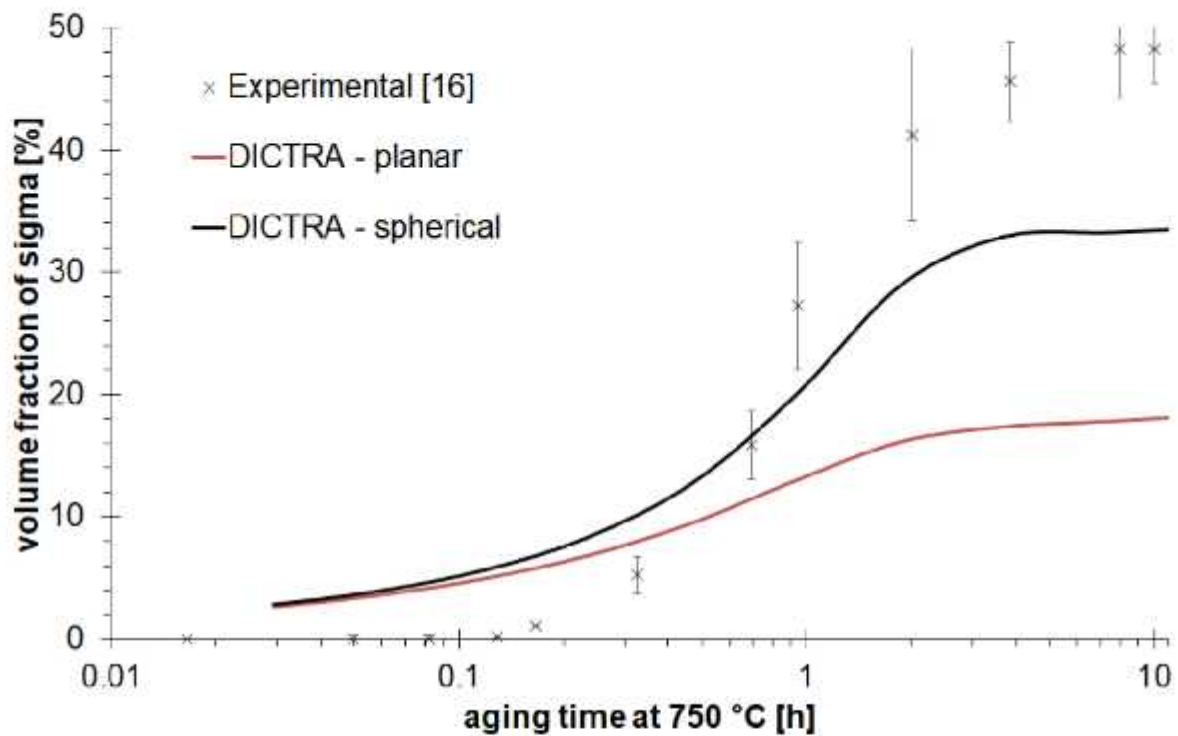**Fig. 4.** Volume fraction of sigma as a function of aging time at 750 °C obtained in DICTRA® simulations using both geometrical models proposed in this investigation, compared to experimental results from [16].
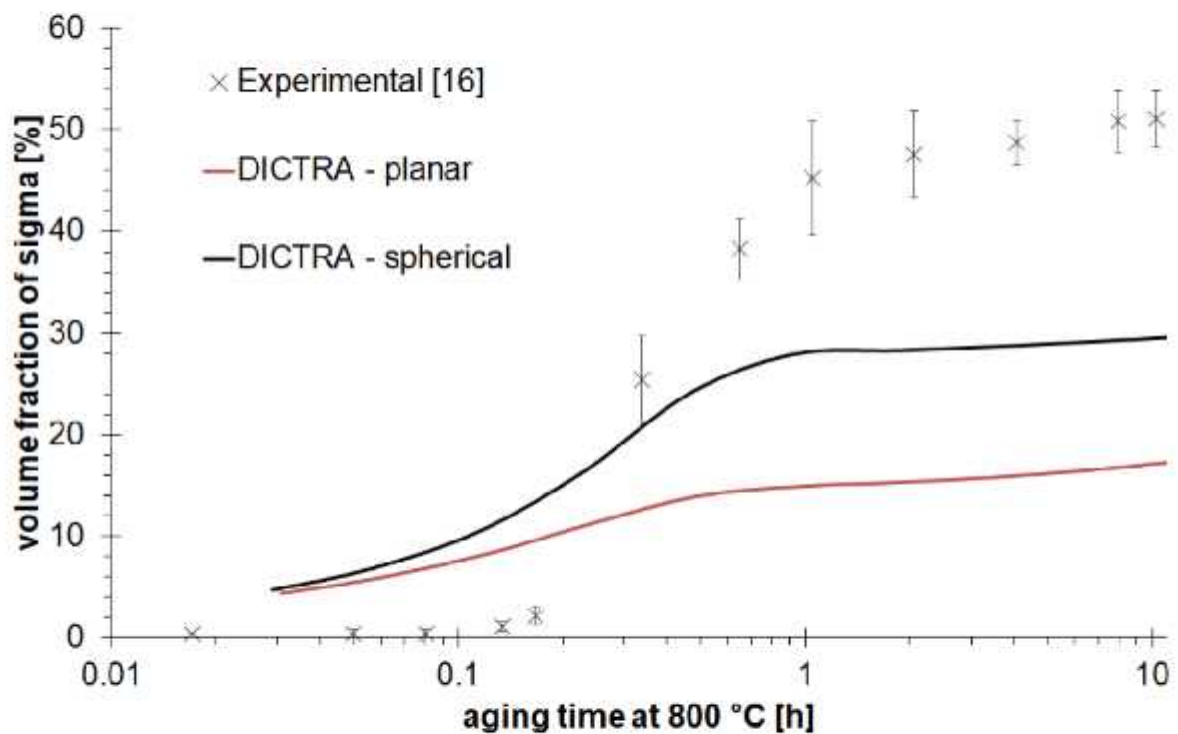

Fig. 5. Volume fraction of sigma as a function of aging time at 800 °C obtained in DICTRA® simulations using both geometrical models proposed in this investigation, compared to experimental results from [16].
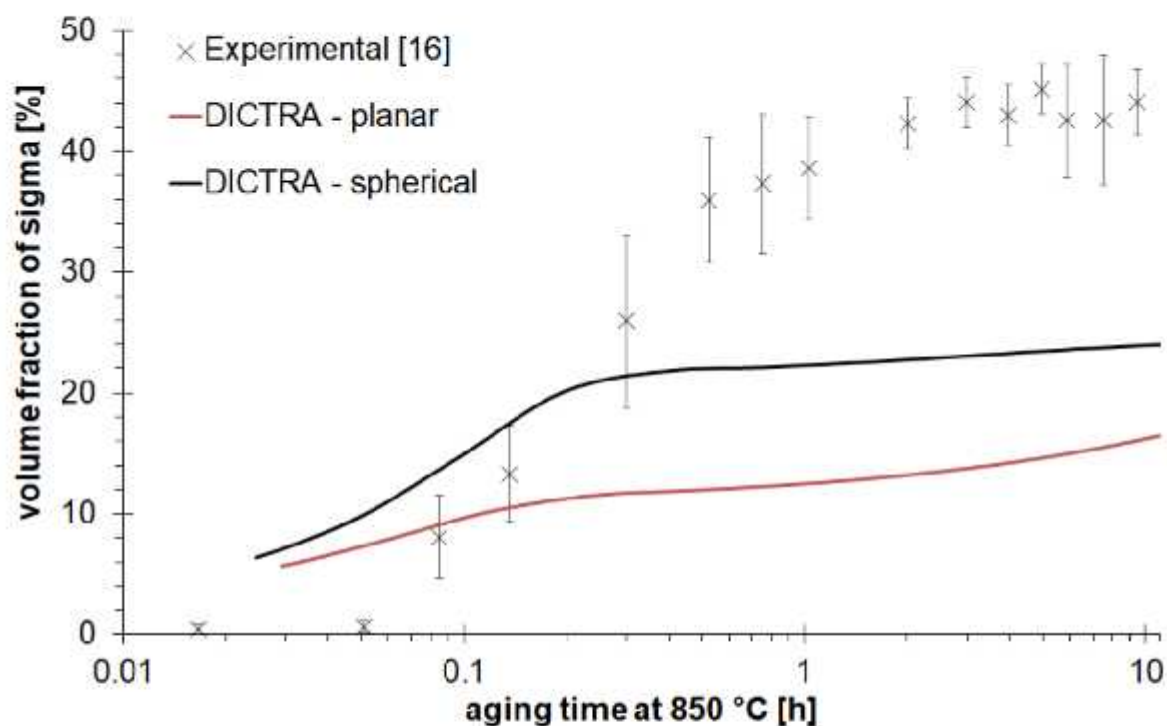
Fig. 6. Volume fraction of sigma as a function of aging time at 850 °C obtained in DICTRA® simulations using both geometrical models proposed in this investigation, compared to experimental results from [16].

Fig. 7. Volume fraction of sigma as a function of aging time at 800 °C obtained in DICTRA® simulations using both geometrical models proposed in this investigation, compared to experimental results from [16].
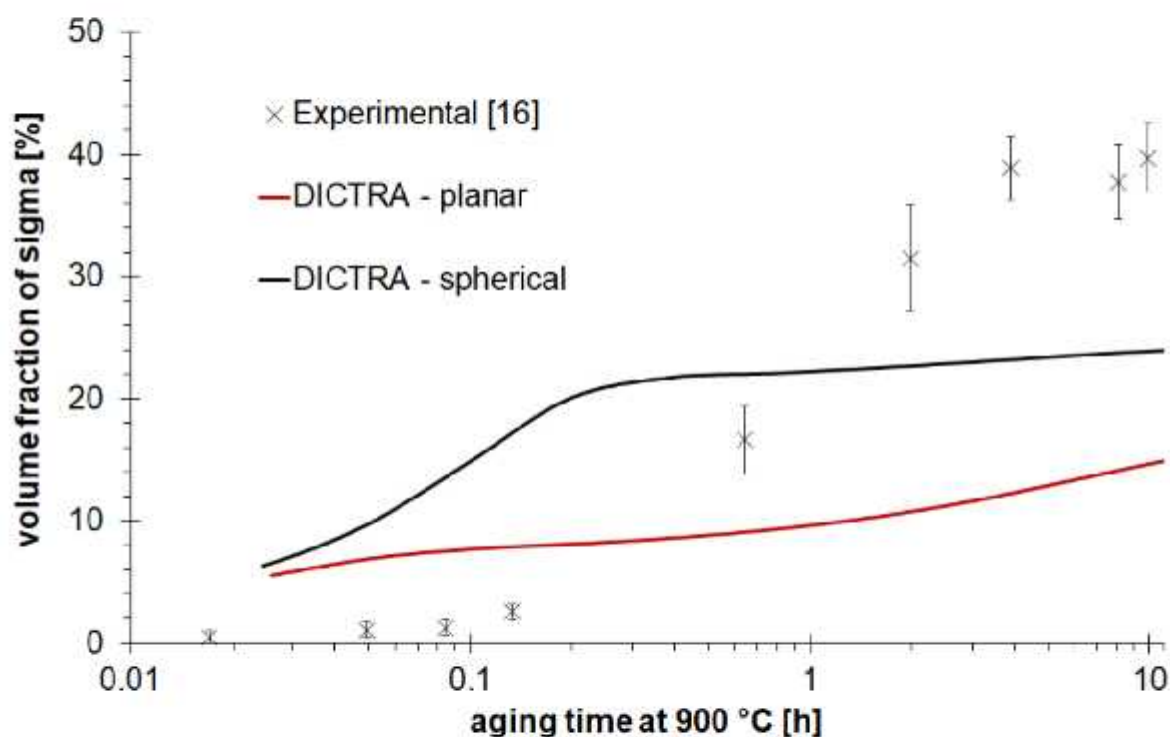
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