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RHEOLOGY OF STELLITE™ 21 ALLOY IN SEMI-SOLID STATE

The main objective of this study was to conduct an analysis of the rheological properties of Stellite™ 21 alloy in the semi-solid state, as the results could be used for identifying the appropriate temperature range for thixoforming of this alloy, and a secondary objective of the experimental work was the development of mathematical model of the alloy's apparent viscosity. Such viscosity models are necessary for numerical simulations of the thixoforming processes. The Stellite™ 21 alloy exhibits high hardness and thus shaping in the semi-solid state is promising route of production of parts from this alloy. Within the confines of experimental work the measurement methods of the rheological properties at high temperatures was developed. They are based on the use of specially designed viscometer equipped with high temperature furnace.

Keywords: thixoforming, rheological properties, viscosity, thixotropy, Stellite™ alloys

1. Introduction

A non-conventional metal alloys processing in the semi-solid state, also known as thixoforming are hybrid manufacturing methodologies based on modified methods normally used in forging or casting processes. Thixoforming processing is successfully used by a number of industries producing aluminium and magnesium alloy parts [1-6]. The technology has numerous applications in the electronic and automotive industries, with parts made of light metal alloys, such as laptop and mobile phone casings, suspension and car engine parts, and so forth. Recently research has been directed towards the practical application of thixoforming in processing high melting point metal alloys [7-10].

The main goal of this work is the analysis of the rheological properties of semi-solid Stellite™ 21 alloy (previously known as Stellite™ 8). This alloy tend to have extremely high melting points due to the cobalt and chromium content. But, the mushy zone is mainly determined by content of tungsten, molybdenum and a small but important amount of carbon [11]. Due to high hardness and toughness of Stellite™ alloys, thixoforming processes is considered as alternative technological route of production of parts made from these alloys [12]. Rheological analysis of high melting point materials in semi-solid state until now mainly concerned steel alloys. Especially, the results obtained by Modigell [13], who analysed flow properties of X210CrW12 up to 1500 °C using rotational viscometer should be taken into consideration. Similar approach was used by Solek [14] where aluminium alloys were investigated. Another approach based on compression test was applied by Cezard [15] and Solek [16]. In order to analyse stress-strain distribution in solidified steel alloys after thixoforming process the flow stress below solidus temperature were also investigated [17].

The basic difficulty within the confines of experimental work was the very high temperatures involved to obtain the semi-solid state in Stellite™ 21 alloy. Such high melting points alloys require using of specialized equipment. The second difficulty is necessity of maintenance of the constant shear rate over long time intervals in the case of analysis of thixotropic properties. Thixotropy is time-dependent fluid behaviour in which the apparent viscosity decreases with time of shearing [18]. This is why a rotational viscometer can be used to investigate the rheological properties of metal alloys. The experimental work consists of two parts. The first part was devoted to analysis of viscosity and the second one to identification of thixotropic properties of Stellite™ 21 alloy.

The results of basic research presented in this paper could be applied in the future in practical applications from technological point of view. Among other things, the knowledge of alloy rheological properties is necessary to determine the main technological parameters such as temperature ranges of forming processes and forces, which should be applied to the shaping dies. It could be successful determined using numerical modelling of thixoforming processes, which require knowledge of the viscosity of the metal alloys being shaped. It is therefore necessary to determine the velocity and pressure fields inside the semi-solid metal filling the dies, as precise determination of this fields, together with the temperature distribution, helps in avoiding possible defects in the final product.

This paper is thetwelfth publication from a thematically related series devoted to process for the conferment of a degree of *doktor habilitowany* on Dr. Krzysztof Sołek, pursuant to the rules laid down in the Act of 14 March 2003 on Academic Degrees and Title and Degrees and Title in the Arts with later changes (Republic of Poland Law). This series concerns thixoforming of high melting point metal alloys.

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2. Experimental methods and material characterization

Rheological analysis of Stellite alloys in the semi-solid state requires application of furnaces having working temperature within the 1250 – 1450 °C range. Then the viscometer FRS1600 designed by the Anton Paar company which consists of a head and a furnace that operates at temperatures in the range 400-1500 °C was used.

The viscosity measurements of the chosen alloy were performed using Searle's method [19-21], i.e. measurements were carried out using a rotational viscometer with a stationary cup (outer cylinder). In this method, the rod is set in motion and the cup is stationary (Figure 1), and the cylinders are concentric, i.e. both cylinders have the same symmetry axis (the rotation axis of the inner cylinder). In this work alumina was used for the tooling because of its resistance at high temperatures and low wettability. Most industrial rheometers work on this principle, named after G.F.C. Searle in 1912, but their main disadvantage is that turbulent flow conditions may materialize while measuring of low-viscosity liquids at high rotational speeds. A photograph of the viscometer is shown in Figure 2.

Fig. 1. Photograph of measurement tools (material - alumina) used in investigations

Measurement of viscosity using FRS 1600 viscometer is limited to momentum values of about 200 mNm, and for safety reasons measurements in this present work were limited to 150 mNm. Viscosity measurements were conducted using appropriate software for controlling the viscometer. The samples were heated above liquidus temperature and the rotating rod was moved down inside the crucible holding the samples before the measurement procedure begun. During measurements, a protective atmosphere is blown into the furnace to avoid oxidation of the liquid sample. The temperature of the sample can be precisely measured using thermocouple located directly below the crucible. Once the measurements are completed, the sample is heated again above the liquidus temperature to eject the spindle from the crucible.

Fig. 2. Photograph of rotational viscometer used in investigations

The chemical composition of investigated Stellite^{TM} 21 alloy is shown in Table 1.

TABLE 1

Chemical composition of Stellite^{TM} 21 alloy in weight %

Element	Co	Cr	Mo	Ni	C
Nominal composition [11]	base	26-29	4.5-6.0	2.0-3.0	0.2-0.35
Investigated alloy	61.36	27.10	5.69	2.93	0.25

The second stage of the experimental work was devoted to the identification of the solid phase content in the material under test as a function of the solidification range temperatures. This involved high temperature DTA analysis conducted using an STA JUPITER 449, Netzsch analyzer. The DTA heating curve and the liquid fraction distribution as a function of temperature for the Stellite^{TM} 21 alloy are shown in Figure 3. The measurements were carried out at a heating velocity of 5 ˚C per minute.

The diagram, shown in Figure 3, shows the approximate solidus and liquidus temperatures, 1295 and 1435 °C, respectively, i.e. a melting range of around 140 °C for this alloy. Such a large temperature difference between solidus and liquidus provides a nice process window for practical industrial applications.

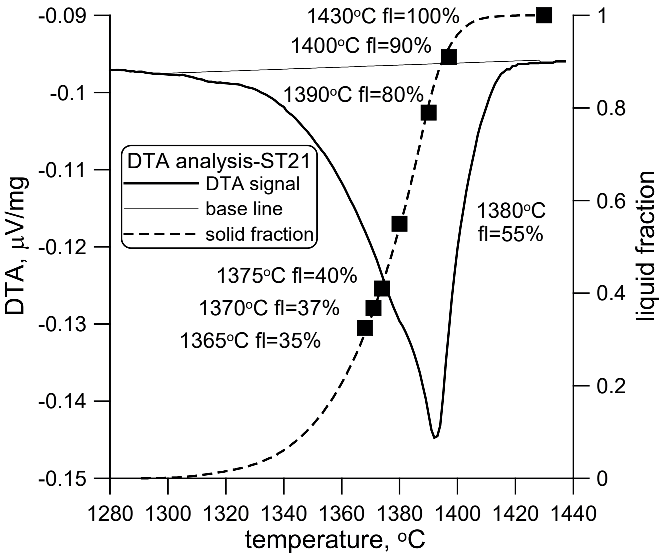

Fig. 3. Content of the solid phase in the Stellite™ 21 alloy as a function of temperature [°C]

3. Viscosity measurements

The first step is concerned with determining the relationship between alloy viscosity and temperature (Figure 4), the expectation being that a decrease in temperature will cause an increase in registered viscosity, especially in the case of semi-solid state metal alloys. The highest viscosity increase appears for temperatures below 1365 °C. This experiment allowed the identification of the maximal material temperature appropriate for the thixoforming process using conventional forging techniques (approximately 1365 oC). The criterion is the value of alloy viscosity, below which the material loses fluidity. Theoretically, the chosen alloy can be subjected to thixocasting processes in the temperature range between 1370 and 1390 oC, using for example high pressure die casting machines, but such processes are not normally executed because of too high material temperature.The values of viscosity depend strongly on the solid fraction in the material, and solid fraction is strongly correlated with the progress of solidification. Another aspect that has influence on the viscosity value is the shear rate (*mech.* the non-dilatational strain rate). Generally, higher temperatures and shear rates cause lower values of material viscosity and thus better castability.

Next, viscosity measurements versus shear rate for selected temperatures (1365, 1370, 1375, 1380, 1390, 1400, 1430 °C) were carried out. Changes of viscosity values were analyzed in the shear rate range between 0.1 and 20s^{-1}; both the temperature changes and the shear rate changes were automatically recorded via a pre-programmed procedure. Figure 5 shows the changes of viscosity of analyzed Stellite™ 21 alloy versus shear rate for different semi-solid range temperatures. Before each viscosity measurement, the sample was sheared with rate of about 5s-1 during the temperature change.

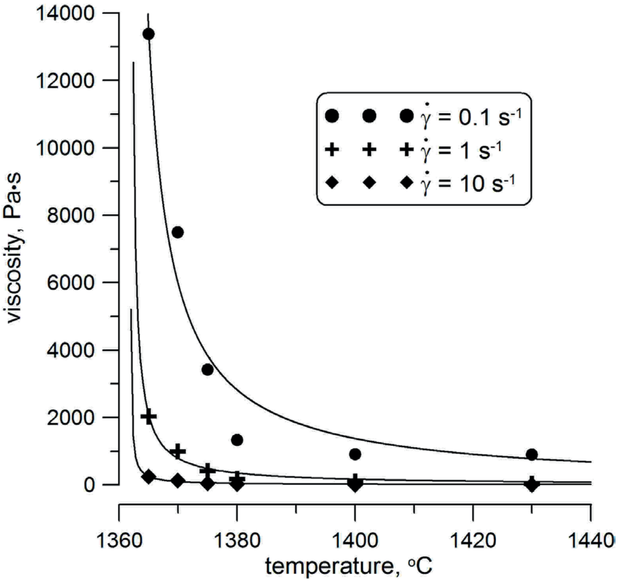

Fig. 4. Relationship between temperature and alloy viscosity

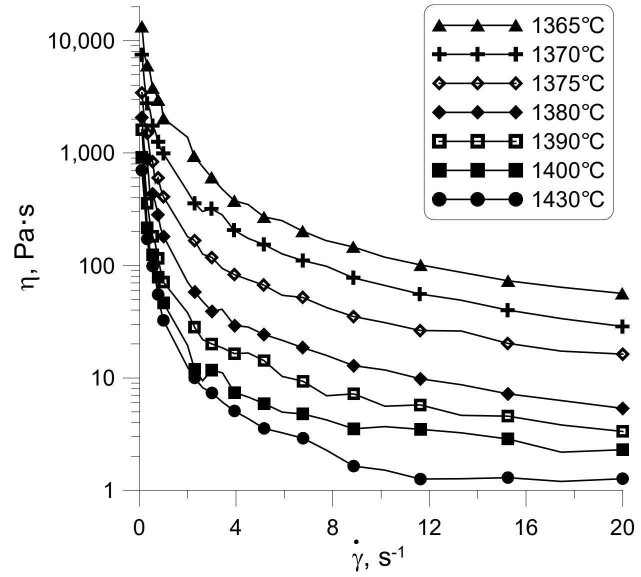

Fig. 5. Viscosity of analysed Stellite™ 21 alloy versus shear rate for different temperatures

4. Thixotropic properties of semi-solid StelliteTM alloy

Figure 6 shows the viscosity changes versus time for different shear rate values for Stellite™ 21. The expectation is that with increasing shear rate, the viscosity decreases over time, as can be observed in Figure 6. When the shear rate decreases one can observe a corresponding increase of viscosity over time. Before analyzing of the thixotropic properties of semi-solid samples, these samples were sheared for some time at about 5 s^{-1}rates in order to obtain the globular microstructures required for thixoforming.

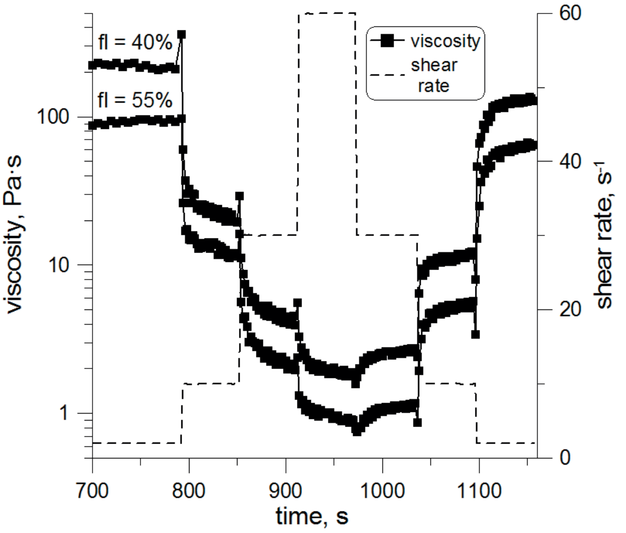

Fig. 6. Viscosity of analyzed Stellite$^{\text{TM}}$ 21 alloy versus time for different values of shear rate and temperature

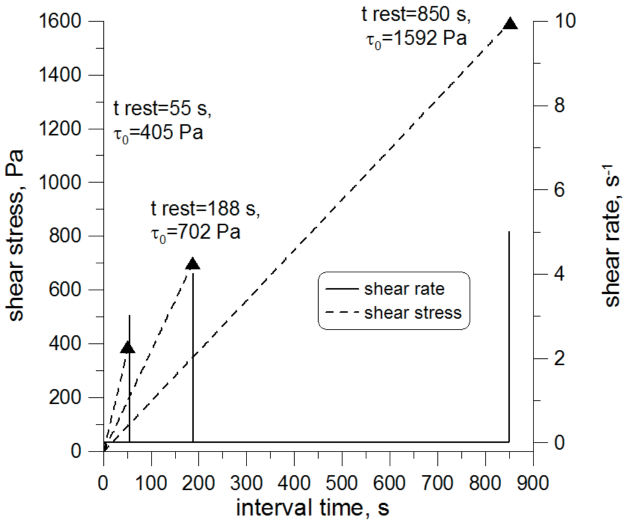

Fig. 7. Shear stress ramps for state of microstructure obtained after shearing with rate of 10 s^{-1} at 1390°C

Next, the influence of resting time on the yield stress was analyzed (Figures 7, 9). Generally, the longer resting time gives the higher yield stress (Figures 8, 10). In this work the values of the yield stress were measured for two different states of microstructure and two different temperatures. The difference in states of microstructure was obtained by two different shear rates of 10 (Figures 7, 8) and 50 s-1 (Figures 9, 10) applied to the alloy before measurements during half an hour. The yield stress measurements were executed for 1380 and 1390 oC (Figure 11). The dots in Figures 7 and 9 associated with shear rate correspond to the moment of the start of material flow and the value of the shear stress recorded in this moment corresponds to the yield stress.

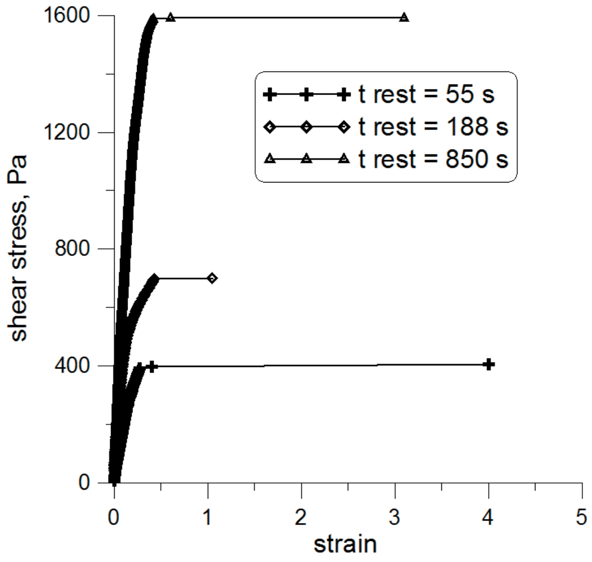

Fig. 8. Flow stress curves for Stellite$^{\text{TM}}$21 alloy for different resting times after shearing with rate of 10 s^{-1}at 1390°C (“t rest” means resting time)

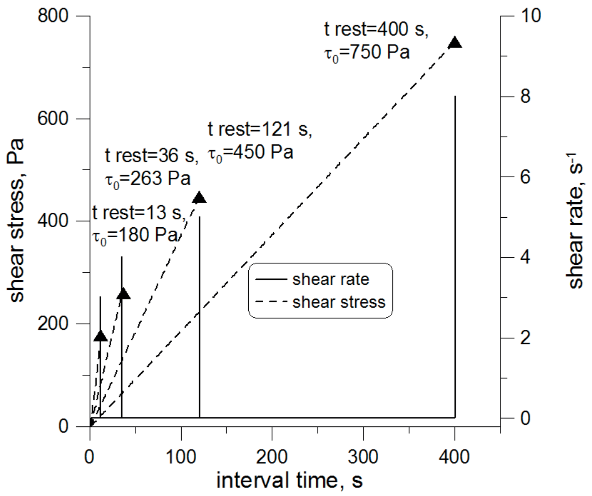

Fig. 9. Shear stress ramps for state of microstructure obtained after shearing with rate of 50 s^{-1} at 1390°C

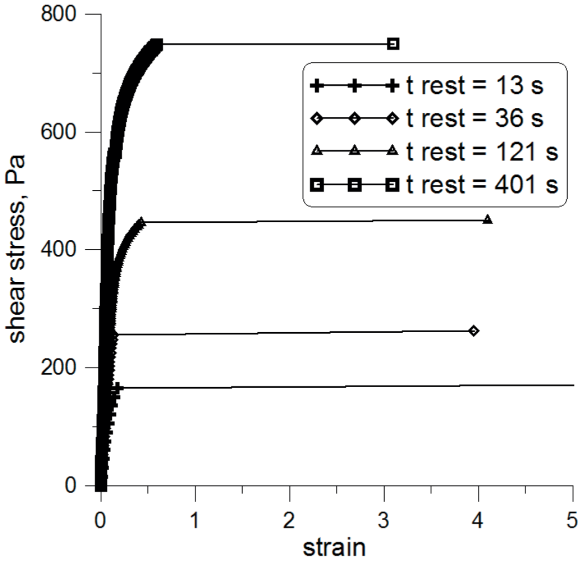

Fig. 10. Flow stress curves for Stellite$^{\text{TM}}$ 21 alloy for different resting times after shearing with rate of 50 s^{-1} at 1390^{o}C (“t rest” means resting time)

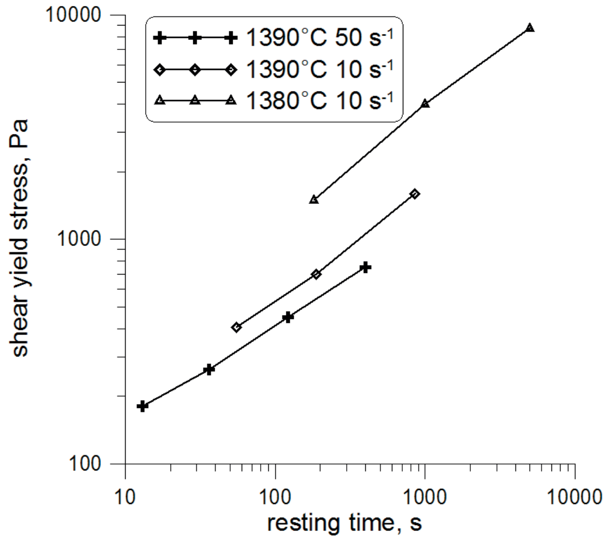

Fig. 11. Values of yield stress for Stellite™ 21 alloy versus resting time for samples at 1390°C and 1380°C previously sheared with rate of 10 and 50 s^{-1}

Measurements carried out in the experimental work shows that an increase of resting time causes an increase of the yield stress. It is due to the rebuilding of the solid skeleton after cessation of the material deformation. It could be observed in Figure 11 where comparison of yield stress values for different values of resting time is shown. Such behaviour of semi-solid Stellite™ 21 alloy is inseparably linked with the thixotropic transition [18]. Additionally, the graph in Figure 11 clearly shows an increase of yield stress with decreasing of temperature, as a result of the greater amount of solid fraction in the alloy. The results of this work support the proposition that a yield point occurs in semi-solid metal alloys.

5. Viscosity equation of Stellite™ 21 alloy in mushy zone

The viscosity measurement results can be used in numerical simulations to determine the progress of filling inside a mould cavity during the thixoforming process. Such simulations can be carried out by applying appropriate viscosity equations to numerical models. One of such viscosity model, used in the ProCAST commercial casting packet, is a Power Law Cut-Off equation [22]:

$$\begin{aligned} \eta &= \eta_0 \cdot (K \cdot \dot{\gamma})^n & \dot{\gamma} &\geq \dot{\gamma}_0 \\ \eta &= \eta_0 \cdot (K \cdot \dot{\gamma}_0)^n & \dot{\gamma} &< \dot{\gamma}_0 \end{aligned} \qquad (1)$$

where:
$\dot{\gamma}$ - shear rate,
$\dot{\gamma}_0$- the critical “cut-off” value of the shear rate,
η_0 - zero shear rate viscosity,
K - K-Factor,
n - power law coefficient.

The values of “Zero viscosity”, “K Factor” and “Power”, which can be temperature dependent, should be experimentally calibrated. The value of n should be negative in order to obtain a decreasing viscosity with an increasing of shear rate, and the K-Factor was set to 1 s in this work.

The estimated parameter values of the PLCO model for the Stellite™ 21 alloy are shown in Figure 12 where the approximation was carried out using the least squares method. The obtained parameter values depend on temperature and can be directly applied in the software to be used in numerical simulations of the thixoforming process. The curves presented on Figure 13 approximate the recorded values of viscosity versus shear rate. It should be mentioned that the PLCO model takes into consideration the shear thinning phenomenon, which occurs in liquid and semi-liquid metals. The phenomenon of thixotropy is partially taken into consideration through the application of the critical “cut-off” value of the shear rate $\dot{\gamma}_0$. According to the model (1) an increase of shear rate causes a decrease of viscosity, but a decrease of shear rate does not cause an increase of viscosity, as it is prevented by replacing the shear rate by its “cut off” value in the model. The values of the power law coefficients are rather high at all investigated temperature ranges, which indicates that the behaviour of Stellite™ 21 alloy is viscous both in semi-liquid and liquid state.

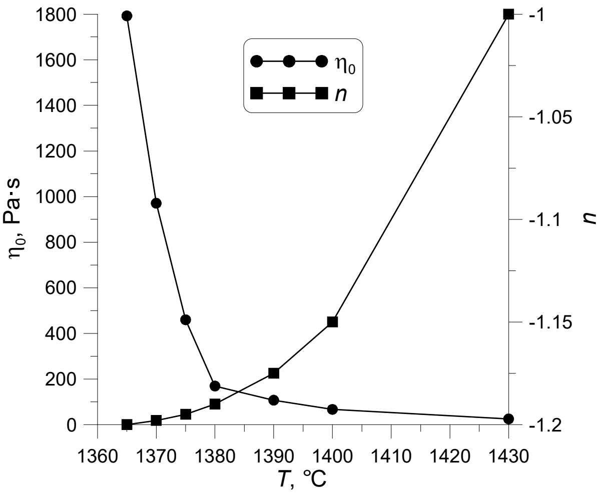

Fig. 12. Graph of zero strain rate viscosity and power law coefficient for Stellite™ 21 alloy as a function of temperature

TABLE 2

Values of zero strain rate viscosity and power law coefficient for Stellite™ 21 alloy versus temperature

T, °C	1365	1370	1375	1380	1390	1400	1430
η_0, Pa·s	1 792.5	970.7	459.7	169.0	106.8	66.6	24.7
n	-1.202	-1.198	-1.195	-1.190	-1.175	-1.150	-1.012

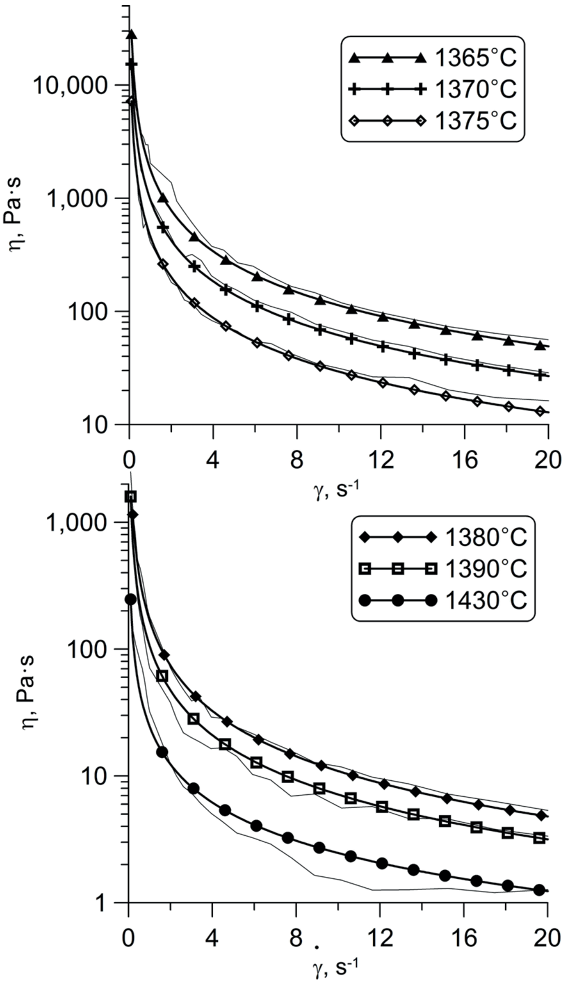

Fig. 13. The curves which approximate (using PLCO model) recorded values of viscosity versus the shear rate

6. Conclusions

The experiments carried out in this work allowed for rheological characterization of StelliteTM 21 alloy in the mushy zone. Both, the shear thinning and thixotropy phenomena were identified.

The thixotropic transition, which causes a decrease in viscosity due to damage of the three-dimensional solid skeleton was identified on the basis of viscosity measurements versus time under constant shear rate. During the experimental work an appearance of the yield stress in the semi-solid StelliteTM 21 alloy was confirmed. Moreover, an influence of a period of the resting time on the yield stress value also proves the thixotropic transition in this alloy.

Results of viscosity measurements were used for identification of a power cut-off model parameters. These one-phase rheological model is used for simulating of thixoforming processes also in commercial software developed for design of casting technologies, such as in the ProCAST package. Obtained parameters allow to calculate the viscosity as a function of the shear rate and the temperature.

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