CONTENTS	Page
Research papers	
<i>T. Berguiga, Z. Boumerzoug</i> Effect of sigma phase precipitation on mechanical behavior and pitting corrosion of duplex stainless steel	4
Andrea Di Schino Effect of austenitic grain size on the phase transformation of a novel 6.5% Cr steel for forged components	18
J. Stoulil, L. Pavlova, M. Kouřil Localised corrosion of stainless steels 316L and 2205 in synthetic bentonite pore water and bentonite slurry	24
O. Chikova, V. Tsepelev, K. Shmakova Viscosity of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi melts of equiatomic compositions	33
H. M. Le, Y. N. Nguyen, D. T. Hoang Truong, H. D. Vu, H. H. Nguyen, K. Q. Dang Preparation of Cu matrix composite reinforced with in-situ nanosized Al <sub>2</sub> O <sub>3</sub> particle powder from metal nitrates	41
H. T. H. Dang, P. T. Thuy, D. M. Ngung, P. Quang, V. Y. Shchukin The deformation of AZ31 magnesium alloy during warm constrained groove pressing	48
L. Kieush, M. Yaholnyk, M. Boyko, A. Koveria, V. Ihnatenko Study of biomass utilisation in the iron ore sintering	55
M. Besterci, K. Sülleiová Theoretical-experimental possibillities of microstructure quantification of dispersion strengthened materials	65
Technical paper	
S. Krivenko Analysis of the quality of moistening of the sinter mix in the drum pelletizer	73

# EFFECT OF SIGMA PHASE PRECIPITATION ON MECHANICAL BEHAVIOR AND PITTING CORROSION OF DUPLEX STAINLESS STEEL

Talha Berguiga<sup>1)\*,</sup> Zakaria Boumerzoug<sup>1)</sup> <sup>1)</sup> LMSM, Department of Mechanical Engineering, University of Biskra, 07000, Algeria

Received: 08.10.2018 Accepted: 21.01.2019

<sup>\*</sup>Corresponding author: e-mail: ber\_talha@yahoo.fr Tel.: +213 661858174 LMSM, Department of Mechanical Engineering, University of Biskra, 07000, Algeria

#### Abstract

The main purpose of this work is to investigate the pitting corrosion behavior of sigmatized duplex stainless steel (DSS) exposed to two different chloride environments: simulated seawater solution and produced water solution. Specimens taken from a commercial DSS (UNS 31803) have been subjected to aging treatments at 850°C for different holding times to achieve different amounts of sigma phase. Metallographic examinations combined with X-ray diffraction technique were employed to follow the microstructure evolution. The pitting potential of the aged samples were determined in simulated seawater solution and produced water solution. It was established that solution treated DSS shows a high pitting corrosion resistance in both test solutions, while serious deterioration of corrosion properties occurs in presence of sigma phase. It was concluded that both sigma phase amount and chloride concentration worsen the pitting potential, the higher sigma content, the lower pitting potential and the higher chloride concentration, the lower pitting potential. SEM observation showed that pitting nucleation occurs preferentially at sigma phase interfaces due to the development of Cr- and Mo-depleted regions around sigma phase. It was also confirmed that the hardness behavior is only affected for long term aged samples.

Keywords: Duplex Stainless Steels (DSS), Sigma, Pitting Corrosion, Simulated Seawater, Produced Water

#### 1 Introduction

Duplex stainless steels (DSS) are Fe-Cr-Ni alloys having an approximately volumetric fraction of 50% ferrite and 50% austenite in their microstructures [1]. DSS combine some characteristics of each of these phases. They have been introduced into the market during 1930s; since that time there has been an accentuated development and rapid spreading of their use [2]. They have been widely used in various industrial sectors due to their higher strength, better weldability, and higher resistance to stress corrosion and pitting [3]. Hence, DSS are attractive material for applications where these properties are desired like in off-shore industries, food industries, chemical industries, paper industries, nuclear industries and in structural applications as well [4, 5]. In particular, the UNS S31803 alloy (also known as steel SAF 2205) is the most widely employed duplex stainless steels nowadays [6,7]. This material grade found widespread use in oil and gas industry, especially for high chloride containing process fluids like oily produced water and injection process systems. The superior properties of the duplex stainless steels come primarily from approximately equivalent amounts of austenite ( $\gamma$ ) and  $\delta$ -ferrite [3].

However, the use of DSS at high temperature is a typical concern to users of duplex stainless steels owing to their susceptibility to the formation of dangerous intermetallic phases, such as  $\sigma$ -

and  $\chi$ -phase, which form after ageing the material in a temperature range over 600 °C [8].Therefore, the use of duplex stainless steels has been usually limited to temperatures not exceeding approximately 500 °C [2]. For instance, according to ASME B31.3 Process Piping Code, the limit of use of UNS31803 Duplex stainless steel grade is 315°C [9].

It is supposed that among intermetallic precipitates, Sigma phase is the most detrimental one, as it causes a considerable drop in toughness as well as corrosion resistance [10]. Even small amounts of sigma phase influence the resistance against most corrosion forms such as pitting, sulfide stress corrosion cracking, intergranular corrosion and hydrogen embrittlement. Consequently, the standard criterion is that no sigma phase is allowed in produced duplex materials [11]. Sigma phase is a Cr-Mo rich hard precipitate which occurs at temperatures between 600-1000°C [4, 12]. The fastest sigma phase precipitation kinetics occurs at 850°C. Once sigma phase is introduced in the microstructure it is difficult to recover the optimum microstructure [13]. The detrimental effect of sigma phase on corrosion resistance was usually associated to the formation of Cr- Mo depleted regions adjacent to sigma phase as a consequence of the eutectoid mechanism generating sigma phase. Concentration can fall below the minimum 12wt. % to 13wt.% of chromium required to ensure the passivation process. Regions with quantities below the minimum Cr range undergo active dissolution and usually corrode at rates close to those of carbon steel and pure iron [14].

From a practical standpoint, sigma phase precipitation can be encountered during the welding process if the cooling rate from 1200 to 800°C is too slow. This usually occurs because either the heat input is too great or the interpass temperature is too high [15, 16]. Incorrectly heat treated DSS may also suffer from sigma phase precipitation. Even though strict specifications and qualification tests are usually required for such grades, the delivery of stigmatized duplex stainless steel components still occurs at times [11].Recently, it was reported that there have been a large number of sigmatized DSS fittings that were delivered and installed in several projects related to offshore production facilities [11].

Numerous studies have been published about the impact of sigma phase on the corrosion resistance. However, most of the available studies have been conducted using a various electrochemical tests in chloride containing solutions (NaCl, CaCl<sub>2</sub>,..). On the other hand there is no published studies examining the electrochemical behavior of sigmatized DSS when exposed to oil and gas field environment. There have been only a limited number of studies related to Super Duplex stainless steel (SDSS) materials tested in a simulated oil field environment [13]. Also the amount of literature on the seawater pitting of aged DSS is limited, more specifically in term of correlation between sigma phase content and pitting potential values.

Given the above facts, this research work was mainly conducted to investigate the pitting corrosion behavior of sigmatized DSS exposed to two different chloride containing environments: simulated seawater solution and produced water solution. It is expected from this study to show the relationship between sigma phase content and pitting potential values. The sigmatized samples were obtained by aging treatment at 850°C during various holding times to introduce varied levels of sigma phase. Therefore, as part of this study, the microstructural evolution after ageing and the effect of sigma phase on the hardness behaviour were also investigated.

#### 2 Materials and experimental procedure

The investigated steel grade in this study is a duplex stainless steel (ASTM 790 UNS 31803) received in the solution treated condition, as a seamless pipe with 3 inch diameter and 5.5mm thickness. The chemical composition of this pipe is given in **Table 1**.

0.013

Elements

wt. (%)

nical cor	npositio	n of the s	studied Ma	aterial				
С	Si	Mn	Р	S	Cr	Mo	Ni	Ν

0.0006

22.400

Table 1 Chen

0.550

1.100

0.0260

Specimens of approximately 20 mm length and 10 mm wide were obtained. A number of samples were kept without any treatment as reference, and the rest of specimens were isothermally aged at 850°C for different holding times ranged from 5 minutes to 360 minutes, in a tubular electric furnace equipped with a temperature controller. At the end of each treatment the specimen was immediately water quenched in order to interrupt the phase transformation process. After heat treatment, the specimens were grinded and polished with alumina powder. Metallographic examinations have been carried out using electrolytic etching in oxalic acid under 2-2.5 V during 10 to 20 seconds [17]. This procedure has the advantage to allow quantitative metallographic analysis of sigma phase. The electrolytic etching employed colors the phases as follows: ferrite-gray, austenite – white, and sigma phase - dark. In addition, the presence of different phases in the specimens was also identified by X-ray diffraction analysis (XRD). Complementary microstructural characterizations using scanning electron microscope (SEM) operated from 7.0 to 30kV have been used for a number of aged samples for further confirmations purpose. The susceptibility of the aged DSS to pitting corrosion was evaluated by potentiodynamic polarization tests. The experiments were conducted in two different chloride solutions: Produced Water solution and 0.5 M NaCl solution simulating seawater chloride concentration. Tests solutions were exposed to laboratory air at room temperature (approximately 25 °C). Produced Water is the recovered water from crude oil production system after separation and filtration. Treated produced water is sent for reinjection into the oil reservoir to increase the oil recovery capacity. The chemical analysis of the produced water used as a test solution for this study is presented in Table 2.

Table 2         Chemical	Analysi	s of	Produced	Water
--------------------------	---------	------	----------	-------

Elements	Cl-	HCO3 <sup>-</sup>	Na <sup>+</sup>	Ca++	$\mathbf{K}^+$
Concentration (mg/l)	28862	61	30765	97	418

The polarization tests were carried out using a potentiostat VOLTALAB PGZ-301 consisting of three electrodes. Platinum was used as the counter electrode and saturated calomel electrode (SCE)) was employed as the reference electrode. The specimens acting as working electrode were embedded in epoxy resin with an approximate exposure area of  $1 \text{ cm}^2$ . Before each test, the exposed surfaces of samples were polished up to 4000 grit finish then rinsed with distillated water and dried in air. The potentiodynamic measurements were performed at a scan rate of 1 mV/S until an anodic current of  $100 \mu \text{A/cm}^2$  was exceeded [18, 19]. The pitting potential (E<sub>pit</sub>) was defined at the potential where the anodic current density exhibited a sharp and sustained increase from the background passive current density [6].

Tested samples in simulated seawater were numbered from "0-SW" to "360-SW" whilst the tested samples in produced water were numbered from "0-PW" to "360-PW", where the numeric characters denote the aging time in minutes. Based on that, specimen identification adopted in this work are listed in **Table 3**. After the polarization tests, the surface of the pitted samples were cleaned and analyzed using SEM observation to examine pit morphology and preferential location.

0.1850

3.150 5.450

In order to investigate the effect of microstructure evolution on hardness behavior of the studied material, Vickers microhardness measurements were performed using 0.3 kg load.

Aging Time (min)	Test solution	Identification
0 (Solution annealed condition)	Simulated Seawater	0-SW
5		5-SW
30		30-SW
60		60-SW
360		360-SW
0 (Solution annealed condition)	Produced Water	0-PW
5		5-PW
30		30-PW
60		60-PW
360		360-PW

Table 3 Specimens identification

## 3 Results And Discussions

## 3.1 Characterization of the investigated material at the as received condition

The microstructure of the studied material in the as received condition is shown in **Fig. 1**, it contains solely austenite and ferrite; ferrite in gray and austenite in white. In addition, the presence of these phases was confirmed by X-ray diffraction analysis as shown in **Fig. 2**, no other phases or precipitates have been detected in the investigated DSS at the as received state.



Fig. 1 Micrograph of the investigated metal at the as received state

The absence of precipitates in the matrix could be explained by the fact that the investigated material was successfully solution treated as required by the manufacturing standard governing the DSS used in this study [20].



Fig. 2 X-Ray diffraction pattern of the studied material in the as received condition

## 3.2 Sigma (σ) phase characterization and formation mechanism after aging treatments at 850 °C

**Fig. 3** shows the microstructure of the aged specimen at 850 °C for 5 minutes holding time. It is well noted that the precipitation of ( $\sigma$ ) sigma phase has been taken place in this treated specimen. Sigma ( $\sigma$ ) phase appears in dark color at the  $\delta / \gamma$  boundaries. It should be noted that  $\chi$  phase precipitates are also present in the matrix of this aged specimen. However, the volume fraction of  $\chi$  was small in comparison with  $\sigma$  phase and it had a far less influence on DSS than  $\sigma$  phase did [21].



Fig. 3 Optical microstructure corresponding to the aged specimen at 850 °C for 5 min

The evidence from transmission electron microscopy also suggests that  $\chi$  phase is much more unstable than  $\sigma$  phase and would eventually transform to  $\sigma$  phase [3]. These findings and assumptions are also applicable for the other aged specimens in this work; therefore  $\chi$  phase

precipitation was not taken in charge in the present study. In fact, when the studied duplex stainless steel specimens were exposed to heat treatment at 850 °C, the original austenite / ferrite balance was disturbed, causing the material to search for a more stable thermodynamic state through the precipitation of sigma phase. The precipitation of sigma phase proceeds according to the following eutectoid mechanism:

$$\delta \rightarrow \gamma_2 + \sigma$$

where  $\gamma_2$  is the so-called secondary austenite [21].

According to Fig. 3 sigma ( $\sigma$ ) phase nucleates preferentially at the  $\delta/\gamma$  interfaces and grows through the adjacent ferrite grain; this feature is more visible on the aged specimens for longer periods as displayed in Fig. 4, which shows SEM image of heat treated sample at 850 °C for 360 min holding time.



Fig. 4 SEM micrograph corresponding to the aged specimen at 850 °C for 360 min

This is a typical feature for sigma phase precipitation in DSS, and it is due to the high interface energy of the  $\delta/\gamma$  interphase boundary, and as many defects concentrate there, it is a beneficial site for the heterogeneous nucleation of the  $\sigma$  phase [17, 22, 23]. When the  $\sigma$  phase nucleates at the  $\delta/\gamma$  interphase boundary, some defects disappear, which releases the free energy of the materials [24]. The noticeable fastest and the high susceptibility of sigma precipitation at 850 °C in the investigated material reported in this study is in good agreement with previous ones, especially the research work conducted by Palmer et al [25] using a synchrotron based in situ X-ray diffraction technique. It was pointed out that sigma  $\sigma$  phase was first observed approximately 40 seconds after the start of the aging treatment at 850 °C. The high susceptibility of the duplex stainless steels to the sigma phase formation is frequently attributed to the ferrite composition, richer in the sigma forming elements (Cr, Mo and Si) and poorer in the elements that are less soluble in sigma (C, N and Ni) than in austenite [17].

### **3.3** Effect of holding time on sigma ( $\sigma$ ) evolution and quantitative analysis

Fig. 5 presents the microstructures of the aged specimens at 850 °C for different holding periods. Sigma phase appears in dark color. It can be clearly seen that increasing the holding

(1.)

time at 850°C has the effect to increase the amount of  $\sigma$  phase. It leads also to the coarsening increase of the  $\sigma$  phase in an irregular shape. The estimated volume fraction of sigma phase by image analysis techniques in function of holding time was plotted in **Fig. 6**.

As it can been seen from **Fig. 6**, the volume fraction of sigma phase start from 1% for a holding time of 5 min to reach 11% after 360 min holding time.



**Fig. 5** Optical micrographs showing the aged specimens at 850°C for (a) 5 min, (b) 60min and (c) 360min



**Fig. 6** Variation of the volume fraction of sigma phase in UNS S31803 as a function of aging time at 850 °C

X-Ray Diffraction analysis has also confirmed this trend. As previously stated, the X-ray diffraction pattern of the solution treated specimen shows ferrite and austenite phase peaks only and does not show any peak corresponding to other phases, however small peaks corresponding to sigma phase have been observed on the aged specimens at 850 °C, these peaks are more detectable in the aged sample for 360 min holding time as reported in **Fig. 7**. With increasing holding time, the intensity of sigma peaks increases and the peak intensity of the ferrite phase compared to the austenite phase decreases, this is directly linked with the decomposition process of ferrite into sigma phase and secondary austenite.



Fig. 7 X-Ray diffraction patterns of samples aged at 850°C

Furthermore, the XRD pattern did not show the  $\sigma$  phase signals in the specimens aged for 30 and 15 min, although there was evidence of its occurrence. This could be explained by the low fraction of the  $\sigma$  phase [21]. Consequently, it can be concluded that all the obtained diffraction peaks are in good agreement with the changes in  $\sigma$  phase ratio during the isothermal treatments.

## 3.4 Influence of sigma phase on pitting potential

Potentiodynamic polarization tests were conducted to evaluate the pitting susceptibility of aged DSS samples with different sigma content levels. **Fig. 8** presents typical polarization curves conducted in 0.5 M NaCl solution.

Basing on the analysis of the polarization curves the pitting potential  $E_{pit}$  values of the different tested samples were determined. The obtained values are shown in the **Table 4**.

Sample identification	0-SW	5-SW	30-SW	60-SW	360-SW
Aging time (min)	0	5	30	60	360
E <sub>pit</sub> (mV/SCE)	1120	980	910	790	560

Table 4 Pitting potentials for the tested samples in Simulated seawater



Fig. 8 Potentiodynamic polarization curves for the aged samples at 850 °C in for different times in simulated seawater solution

It can be seen from **Table 4** that the pitting potentials of tested samples decrease markedly with increasing of aging time from 1120 mV (SCE) of the solution treated sample to 560mV (SCE) of the aged for 360 min. It was previously established in this research work that the increase of the aging time has the effect to increase the sigma phase ratio. So it's clear that the decrease of pitting corrosion resistance in the aged DSS samples is directly attributed to the formation of sigma phase and its volume fraction. Even about 3.1 % of sigma phase which corresponds to the aged sample for 30 min can affect dramatically the pitting resistance of the alloy. On the other hand, the un-aged sample show the highest pitting potential value, supporting the standard recommendation of using DSS in the solution treated condition with no sigma phase content. Actually, it is well documented in the literature that the resistance of this material to localized corrosion is mainly due to the higher content of chromium and molybdenum which protect the DSS by forming and stabilizing the passive film. The decrease in pitting potential as a result of sigma phase formation has been explained by many authors, and it was related to chromium and molybdenum depletion in the zones surrounding sigma phase [6, 21, 26, 27]. During the formation of sigma phase, Cr and Mo diffused from the ferrite phase to the growing sigma phase, thus causing localized depletion areas in Cr and Mo around the sigma phase. These areas containing lower concentration of Cr and Mo and higher amount of Ni became unstable and transformed into secondary austenite [21]. These Cr- and Mo-depleted areas surrounding sigma phase become susceptible to pitting attack and thus a reduction on pitting potential is registered.

The lower molybdenum and chromium content is not the only factor for being prone to corrosion. The neighborhood of the more noble phases will enhance the anodic dissolution of the new formed secondary austenite [28].

This behavior of decrease in corrosion resistance due to the increase in aging time was also established in the tested samples in Produced Water as outlined hereafter.

The polarization curves for the tested specimens in produced water solution are presented in **Fig. 9**. Following the same methodology adopted previously for the tested specimens in

simulated seawater solution, the pitting potential values have been determined and listed in the **Table 5**. The presented data suggest that the pitting potential of the various tested samples show a clear dependence on the aging time. As expected, for high aging time, and consequently high sigma volume fraction, low pitting potential is registered. However, it is well noted that for same aging time a lower pitting potential is found for tested sample in produced water solution.

The lower corrosion resistance of aged DSS in produced water solution can be explained by the higher chloride content in this solution. The other chemical species of the produced water solution shown in **Table 2** do not appear to have a significant impact on the pitting corrosion behavior. In fact the chloride concentration in the simulated seawater solution (0.5M NaCl solution) is about 17725 ppm while in the produced water solution is about 28862 ppm. This confirms that the pitting potential depends on both sigma phase content and the chloride concentration. For chloride, three different models are frequently quoted to explain its effects on pitting: adsorption leading to local film dissolution, penetration of anions in the film leading to weakening of the oxide bonds, and rupture of film at defects, such as cracks and dislocations [18].



Fig. 9 Potentiodynamic polarization curves for the aged samples at 850°C in for different times in Produced Water solution

Table 5 Fitting potentials for the tested samples in Froduced Water									
Sample identification	0-PW	5-PW	30-PW	60-PW	360-PW				
Aging time (min)	0	5	30	60	360				
E <sub>pit</sub> (mV/SCE)	1024	950	720	570	450				

 Table 5 Pitting potentials for the tested samples in Produced Water

On the other hand the obtained results suggest that the un-aged sample demonstrate an acceptable pitting resistance when exposed to produced water test solution, confirming the indication that this material grade when successfully heat treated is highly suitable for use for produced water process fluids, even at a high level of chloride concentration. Therefore, caution

14

is needed by DSS manufacturers and users to ensure a high quality of DSS products during processing, machining, heat treatments and welding to avoid sigma phase formation.

## 3.5 Pitting morphology & its relation to sigma phase

To understand the effect of aging on pits morphologies and the relation between sigma phase and pitting nucleation sites, the pitted samples have been analyzed using SEM observations with secondary electron image (SEI) and backscattered electron image (BEI). **Fig. 10** displays the typical SEM images of pitied samples after polarization tests in simulated seawater solution. Small size isolated pits are observed in the solution treated sample while sever pitting corrosion is registered in the aged sample for 60 min with a larger size pits compared to the solution treated sample. In particular **Fig. 10**(d) presents a "lacy pattern pit morphology", similar to the observations made by other research groups [26, 27]. It is well observed also that pits initiated close to sigma phase regions which is an indication that pits nucleate preferentially at sigma phase interfaces. This finding can be explained by the fact that sigma phase precipitation could lead to the development of Cr- and Mo-depleted zones around the sigma phase, formed by secondary ferrite and by secondary austenite. Thus pit growth occurs as selective corrosion of the metallic matrix surrounding the sigma phase, which is explained by the presence of Cr- and Mo-depleted ferrite or austenite phases surrounding the sigma, as a consequence of the lower corrosion resistance of those secondary phases [26].



(a)

(b)



Fig. 10 SEM images of pitted samples (a) and (b) solution treated sample, (c) and (d) aged samples for 60 min at 850 °C

#### 3.6 Impact of sigma phase on hardness

The results of the hardness measurement of the treated samples are plotted on **Fig. 11**. The general trend observed in this figure stipulates that when the holding time is increased the hardness is increased consequently; this is due to sigma phase volume ratio present in the matrix of the aged samples. The higher sigma phase amount, the higher hardness value. In fact, the hardness of the  $\sigma$  phase is significantly greater than that for the  $\chi$  phase; ferrite or austenite [29], therefore the increase in the hardness is attributed to the increasing in concentration of the  $\sigma$  phase. However, it was noted that short-term aging at 850 °C results in little decrease in hardness for short-term aged samples is probably associated to reduction in solute contain of ferrite to nucleate sigma phase, particularly reduction in chromium and molybdenum content [30]. But generally speaking it is well established that the hardness is not a sensitive measure for low sigma content as indicated by Nilsson et al [31].



Fig. 11 Microhardness evolution as a function of aging time at 850°C for the studied DSS (UNS S31803)

### 5 Conclusions

In this work the sigma phase precipitation in UNS 31803 DSS during isothermal aging at 850C° has been investigated. The effect of sigma phase on pitting corrosion resistance and hardness behavior was also studied. It constitutes a good background for understanding the quantitative correlation between sigma phase amount and corrosion resistance.

The principal conclusions that can be drawn from this work are the followings:

- The microstructure evolution of the aged material has been interpreted in terms of (σ) sigma phase precipitation on the basis of image analysis and XRD. The obtained diffraction peaks are in good agreement with the analysis of metallographic images of aged DSS samples. The results show that the duplex stainless steel UNS31803 is very sensitive to the formation of sigma phase at 850 °C.
- The evidence shows that short-term aging at 850°C of UNS S31803 DSS leads to sigma phase precipitation following a preferential nucleation at ferrite / austenite interfaces.

- Increasing the holding time at 850 °C has the effect to increase the volume fraction and particle size of (σ) sigma phase. The higher holding time, the higher amount of (σ) sigma phase.
- Solution treated DSS samples show a high pitting corrosion resistance in both test solutions, simulated sea water and produced water, making this material grade highly suitable for use in chloride containing environments. However, serious deterioration of corrosion properties occurs in presence of sigma phase which may be introduced into the DSS microstructure in most cases as a result of inappropriate heat treatment. The results show that even about 3.1 % of sigma volume fraction is sufficient to cause a significant reduction on the pitting corrosion resistance of the UNS 31803 DSS.
- It was concluded that both sigma phase amount and chloride concentration worsen the pitting potential. The higher sigma content, the lower pitting potential and the higher chloride concentration, the lower pitting potential.
- Pitting nucleates preferentially at sigma phase interfaces for the aged specimens due to the development of Cr- and Mo-depleted zones around the sigma phase, formed by secondary ferrite and by secondary austenite.
- Hardness is not a sensitive parameter for low amounts of sigma phase. Hardness is significantly affected by higher sigma phase content.

## References

- M. E. Arikan, R. Arikan, M. Doruk: International Journal of Corrosion, Vol. 2012, 2012, p. 1-10, DOI: 10.1155/2012/651829
- S.K. Ghosh, S. Mondal: Materials Characterization, Vol. 59, 2008; No. 12, p. 1776-1783, DOI:10.1016/j.matchar.2008.04.008
- [3] K. L. Weng, T. H. Chen, J. R. Yang: Bulletin of the College of Engineering, N.T.U, Vol. 89, 2003, p. 45-61
- [4] P. Paulraj, R. Garg: Advances in Science and Technology Research Journal, Vol. 9, 2009, No. 27, p. 87-105, DOI: 10.12913/22998624/59090
- [5] R. T. Loto: Journal of Materials Research and Technology, Vol. 6, 2017, No.3, p. 203-212, DOI: 10.1016/j.jmrt.2016.11.001
- [6] H. M. Ezuber, A. El-Houd, F. El-Shawesh: Desalination, Vol. 207, 2007, p. 268–275, DOI:10.1016/j.desal.2006.05.021
- [7] K. W. Chan, S. C. Tjong: Materials, 2014, Vol. 7, p. 5268-5304, DOI: 10.3390/ma7075268
- [8] I. Calliari, M. Breda, E. Ramous, M. Magrini, G. Straffelini: Effect of isothermal heat treatments on Duplex Stainless Steels impact toughness, In: Convegno Nazionale IGF XXII, 1-3 Luglio, Roma, Italia, 2013, p. 56-65
- [9] The American Society of Mechanical Engineers, ASME B31.3, ASME Code for Pressure Piping, B31.3 - 2004
- [10] H. Keshmiri, A. Momeni, K. Dehghani, G. R. Ebrahimi, G. Heidari: Journal of Materials Science & Technology, Vol. 25, 2009, No. 5, p. 597-602
- [11] T. Mathiesen, C. Jensen: Rapid Corrosion Test for Detecting Intermetallic Phases in Duplex Stainless Steels, In: NACE Corrosion 2013, Orlando, FL, Paper 02583, March 2013, p. 1-12
- [12] I. J. Marques, A. A. Vicente, J. A. S. Tenório, T. F. A. Santos: Materials Research, Vol. 20, 2017, No. 2, p. 152-158, DOI: 10.1590/1980-5373-MR-2016-1060
- [13] J. R. Saithala, S. Mahajanam, H. S. Ubhi, J. D. Atkinson: In: CORROSION 2012 Conference & Expo- NACE, C2012-0001272, 2012

- [14] M. Martins, L. C. Casteletti: Material Characterization, Vol. 60, 2009, No. 2, p. 150-115, DOI: 10.1016/j.matchar.2008.12.010
- [15] J. H. Potgieter: British Corrosion Journal, Vol. 27, 1992, No. 3, p. 219-223
- [16] J. A. Castro, E. M Oliveira, D. S. S. Almeida, G. S. Fonseca, C. R. Xavier: Materials Research, Vol. 20, 2017, No. 1, p. 153-161, DOI: 10.1590/1980-5373-MR-2017-0384
- [17] D. M. E. Villanueva, F. C. P. Junior, R. L. Plaut, A. F. Padilha: Materials Science and Technology, Vol. 22, 2006, No. 9, p. 1098-1104, DOI: 10.1179/174328406X109230
- [18] C. Dong, H. Luo, K. Xiao, T. Sun, Q. Liu, X. Li: Journal of Wuhan University of Technology-Mater. Sci. Ed, Vol. 26, 2011, No. 4, p. 641-647, DOI: 10.1007/s11595-011-0283-4
- [19] N. Ebrahimi, M.H. Moayed, A. Davoodi: Corrosion Science, Vol. 53, 2011, No. 4, p. 1278–1287, DOI: 10.1016/j.corsci.2010.12.019
- [20] ASTM A790: Standard Specification for Seamless and Welded Ferritic/Austenitic Stainless Steel Pipe, An American National Standard, 2000
- [21]B. Deng, Z. Wang, Y. Jiang, H. Wang, J. Gao, J. Li : Electrochimica Acta, Vol. 54, 2009, No. 10, p. 2790-2794, DOI: 10.1016/j.electacta.2008.11.038
- [22] J. Michalska, M. Sozańska: Materials Characterization, Vol. 56, 2006, No. 4, p. 355–362, DOI: 10.1016/j.matchar.2005.11.003
- [23] R. Magnabosco: Materials Research, Vol. 12, 2009, No. 3, p. 321-327, DOI: 10.1590/S1516-14392009000300012
- [24] C. C. Hsieh, W. Wu: ISRN Metallurgy, Vol. 2012, 2012, p. 1-16, DOI: 10.5402/2012/732471
- [25] T.A. Palmer, J.W. Elmer, S.S. Babu, E.D. Specht: Direct Observations of Sigma Phase Growth and Dissolution in 2205 Duplex Stainless Steel, In: Trends in Welding Research, Pine Mountain, GA, United States, May 16, 2005 through May 20, 2005, p. 1-8
- [26] R. Magnabosco, N. A. Falleiros: CORROSION, Vol. 61, 2005, No. 2, p. 130-136, DOI: 10.5006/1.3278167
- [27] D. C. Santos, R. Magnabosco, C. M. Neto: CORROSION, Vol. 69, 2013, No. 9, p. 900-911, DOI: 10.5006/0768
- [28] M. Pohl, O. Storz, T. Glogowski : Materials Characterization, Vol. 58, 2007, No. 1, p. 65-71, DOI: 10.1016/j.matchar.2006.03.015
- [29] R. A. Akisanya, U. Obi, N. C. Renton: Materials Science and Engineering A, Vol. 535, 2012, p. 281-289, DOI: 10.1016/j.msea.2011.12.087
- [30] R. Magnabosco, L. E. Oiye, C. K. Sutto : Microhardness of UNS S31803 (SAF 2205) duplex stainless steel after isothermal aging between 700°C and 900°C, In: 17th International Congress of Mechanical Engineering, São Paulo, November 10-14, 2003, p. 1-7
- [31]J. O. Nilsson, P. Kangas, T. Karlsson, A. Wilson: Metallurgical and Materials Transactions A, Vol. 31A, 2000, No. 1, p. 35-45, DOI: 10.1007/s11661-000-0050-1

# EFFECT OF AUSTENITIC GRAIN SIZE ON THE PHASE TRANSFORMATION OF A NOVEL 6.5% Cr STEEL FOR FORGED COMPONENTS

Andrea Di Schino<sup>1)\*</sup> <sup>1)</sup>Università degli Studi di Perugia, Dipartimento di Ingegneria, Perugia, Italy

Received: 17.10.2018 Accepted: 21.02.2019

\*Corresponding author: andrea.dischino@unipg.it, Tel.+39 0744 492953, Dipartimento di Ingegneria, Università di Perugia, Via G. Duranti, 01625 Perugia, Italy

## Abstract

In this paper the effect of quenching and tempering (Q&T) thermal treatment on mechanical properties of a novel 6.5% Cr steel for forged components is studied. The main innovation is in the increased hardenability following the higher Cr content with respect to the more common 5% Cr steel allowing to lower the content of other chemical elements aimed to achieve the target mechanical properties. Following to the high intrinsic hardenability of such steel based on the Cr content a poor effect of prior austenite grain size should be expected after quenching. Aim of this work is to evaluate such effect and to analyse the dependence of mechanical properties on it.

Keywords: Cr content, heat treatment, mechanical properties

## 1 Introduction

Mechanical properties in steel can be improved by adding alloying elements. Among them the most commonly used are chromium and molybdenum. Different strengthening mechanism can be activated depending on final product properties to be targeted. The standard methods used for strengthening steels are [1, 2]:

- microstructure refinement,
- solution hardening,
- dislocation strengthening,
- precipitation hardening.

It has been reported that the tensile properties are strongly dependent on grain size and such mechanism should increase the yield strength up to three times [3-4]. Moreover, such method can allow the best strength/toughness combination [5-7]. Solution hardening allows to increase fatigue and high temperature behavior [8-10]. Anyway, both methods could be difficult or quite expensive since are affected by the cost of the elements to be added at the steel composition. This paper will focus mainly on the quenching and tempering strategy adopted for steels for forgings [11-13] with enhanced Cr content. Quenching and tempering (Q&T) is one of the most common heat treatment processes after forging. Although forging could increase the product strength, usually the actual hardness values are still poor. Heat treatments are generally carried out after forging aimed to achieve the target mechanical properties. It is the combination of these two processes (forging and heat treatment) that allows to achieve a harder, tougher part that's easier weldable and ductile than ordinary carbon steel. However, producing forgings using the Q&T is inefficient and deleterious to the environment and alternative routes to high strength

forgings have been studied for decades [14]. For flat C-Mn steel rolled product the addition of microalloying elements is usually adopted to increase tensile properties [15-20]. Thus, vanadium micro-alloying is predominant in these steels, although growing importance is being placed on dual additions of vanadium with lower levels of niobium. Nitrogen additions are useful to enhance precipitation strengthening in the vanadium applications [21-24]. Moreover, increased yield strength can be achieved by improving hardenability and Cr is usually added with increasing material costs.

These micro-alloying strategies are increasingly employed to enhance strength and performance, or to reduce the number of heat-treating steps while maintaining adequate mechanical performance.

#### 2 Experimental materials and methods

A steel with chemical composition 0.30% C – 0.70% Mo – 6.50% Cr – 0.65% Mn, measured by Quantitative Spectroscopy Analysis, is considered in the following. The steel was manufactured by Electroslag Remelting process (ESR) resulting in higher internal quality ingots. From the ingot, specimens have been cut for Continuous Cooling Temperature (CCT) curves determination. CCT curves were determined by means of dilatometry measurements carried out on 5 mm length 1 mm diameter specimens, with controlled cooling rate. After cooling all specimens were analyzed for hardness and microstructure by Light Microscopy (LM). Phase transformations have been studied and, following to it, quenching and tempering (Q&T) treatments have been performed starting from two different austenitization temperatures (980°C and 1200°C) followed by cooling at the rate defined by CCT and tempering at different temperatures. Microstructure analysis and hardness measurements of heat treated specimens have been carried out by means of Light Microscopy (LM) after 4% Nital etching and 2 Kg Vickers indenter (HV<sub>2</sub>). Room temperature tensile tests were carried out according to ISO 6892-1 specification.

#### 3 Results

Dilatometric curves of the selected steel after austenitization at 980°C and 1200°C are reported in **Fig. 1**. The built CCT diagram based on such curves are shown in **Fig. 2**.







**Fig. 2** CCT diagrams of the selected steel (red curve: austenitizationa at 980°C; blue curve: austenitizationa at 1200°C)

Results reported in **Figs. 1** and **2** show that for such high Cr steel, a negligible austenitization temperature effect is found to be on the cooling behaviour, following the high intrinsic hardenability, even if a strong difference holds is found in terms of prior austenitic grain size (**Fig. 3**).



**Fig. 3** Austenitic grain size of two specimens after austenitization at 980 °C (a) and 1200 °C (b)

Based on results reported in Fig. 2, specimens were austenitized at 980°C, air cooled to achieve a fully ferritic-pearlitic microstructure (reproducing what is found in forgings); specimens were

tempered in the range  $540^{\circ}C - 660^{\circ}C$  for 30 minutes holding time. The microstructure obtained after cooling is reported in **Fig. 4**. It is fully ferritic and pearlitic, as expected following **Fig. 1**. Hardness measurements performed on quenched and tempered materials are shown in **Fig. 4**. Results show that values do not significantly change in the range of the tempering temperature as expected in the case of microstructure mainly constituted by ferrite and pearlite (**Fig. 5**). Results of tensile tests Q&T materials after tempering at  $640^{\circ}C$  are reported in **Table 1**.



**Fig. 4** Microstructure after austenitization and cooling: austenitization temperature = 980°C



Fig. 5 Effect of tempering on hardness. Austenitization time: 30 min, tempering time: 30 min

1	tuble 1 Tenshe properties of material at	asterntized at 900 C	und tempered ut 1	010 0
	Austenitization temperature (°C)	R <sub>m</sub> [MPa]	R <sub>p 0.2</sub> [Mpa]	А,%
	980	966.4	739.9	18.3
	1200	737.6	407.6	20.3

Table 1 Tensile properties of material austenitized at 980°C and tempered at T=640°C

#### 4 Discussion

Results show that in the case of 6.5% Cr steel, following the high intrinsic hardenability, the austenitic grain size effect on microstructure after cooling is really poor. Based on this result the same behaviour in terms of microstructure is found after austenitization at 1200 °C (typical forging process temperature) or 980 °C (typical heat temperature applied to final product). It is worth to be mentioned that in many cases this should allow to avoid the final Q&T treatment, just adopting the material in the as-forged condition. Nonetheless, the adoption of a final heat treatment (anyway independent on tempering temperature) should allow to increase the tensile properties, as a result of the ferrite refinement following the austenite grain size refining effect.

#### 5 Conclusion

In this work the effect of quenching and tempering (Q&T) thermal treatments on mechanical properties of a C-Mn steel with 6.5% Cr for forged components has been studied on a laboratory scale. Results show that the microstructure obtained after Q&T treatments is almost totally ferritic and pearlitic and the hardness of Q&T samples does not change in the range of 540°C to 660°C of tempering temperature. Results show the possibility to increase tensile properties if such steel based on a Q&T process also in absence of an effect due to the austenitisation temperature.

#### References

- [1] T. Kvackaj, I. Mamuzic: Metalurgija, Vol. 45, 2006, No. 1, p. 51-55
- [2] T. Kvackaj et al.: Acta Polonica Physica A, Vol. 126, 2014, No. 1, p. 184-185, DOI: 10.12693/APhysPolA.126.184
- [3] A. Di Schino, J.M. Kenny, I. Salvatori, G. Abbruzzese: Journal of Materials Science, Vol. 22, 2001, p.593, DOI: 10.1023/A:1004856001632
- [4] R. K. Ray, J. J. Jonas, R. E. Hook: International Materials Reviews, Vol. 39, 1994, p.129, DOI: 10.1179/imr.1994.39.4.129
- [5] A. Di Schino, C. Guarnaschelli: Materials Science Forum, Vol. 638-642, 2010, p.3188, DOI: 10.4028/www.scientific.net/MSF.638-642.3188
- [6] R. Song, D. Ponge, D. Raabe, J. G. Speer, D. K. Matlock: Materials Science and Engineering A, Vol. 441, 2006, p.1, DOI: 10.1016/j.msea.2006.08.095
- [7] F. G. Caballero, H. K. D. H. Bhadeshia: Current Opinion in Solid State and Materials Science, Vol. 8, 2004, p.251, DOI: 10.1016/j.cossms.2004.09.005
- [8] A. Di Schino, M. Barteri, J.M. Kenny: Journal of materials Science Letters, Vol. 22, 2003, p.1511, DOI: 10.1023/A:1026155215111
- [9] A. Di Schino, J.M. Kenny, M. Barteri: Journal of materials Science Letters, Vol. 22, 2003, p.691, DOI: 10.1023/A:1023675212900
- [10] M. Corradi, A. Di Schino, A. Borri, R. Rufini: Construction and Building Materials, Vol. 181, 2018, p. 335, DOI: 10.1016/j.conbuildmat.2018.06.034
- [11] A. J De Ardo, C. I Garcia, M. Hua: Metallurgia Italiana, 2010, p. 5
- [12] A. Di Schino, L. Alleva, M. Guagnelli: Materials Science Forum, Vol. 715-716, 2012, p. 860, DOI: 10.4028/www.scientific.net/MSF.715-716.860
- [13] A. J De Ardo: International Materials Reviews, Vol. 48, 2003, p. 371
- [14] A. Steinen, K. Vetterm: Harterei Techn Mitt, Vol. 29, 1974, p. 169
- [15] A. Di Schino, P. Di Nunzio, Acta Metallurgica Slovaca, Vol. 23, 2017, p. 62, DOI: 10.12776/ams.v23i1.852

- [16] A. Di Schino, P.E Di Nunzio: Materials Letters, Vol. 186, 2017, p. 86, DOI: 10.12776/ams.v23i1.836
- [17] A. Di Schino: Acta Metallurgica Slovaca, Vol. 22, 2016, p. 266, DOI: 10.12776/ams.v22i4.815
- [18] A. Di Schino, J.M. Kenny, G. Abbruzzese: Journal of materials Science, Vol. 37, 2002, p.5291, DOI: 10.1023/A:1021068806598
- [19] A. Di Schino, P.E: Di Nunzio, L. Turconi: Materials Science Forum, Vol. 558-559, 2007, p. 1435, DOI: 10.4028/0-87849-443-x.1435
- [20] Y.Li, J.A. Wilson: ISIJ International, Vol. 44, 2004, p.1093, DOI: 10.2355/isijinternational.44.1093
- [21]G. Bregliozzi, S.I. Ahmed, A. Di Schino, J.M. Kenny, H. Haefke, Tribology Letters, Vol. 17, 2004, p. 697, DOI: 10.1007/s11249-004-8075-z
- [22] D.T. Llewllyn: Ironmaking and Steelmaking, Vol. 20, 1993, p. 338
- [23] A. Di Schino, M. Longobardo, G. Porcu, G. L. Turconi, L. Scoppio: NACE- International Corrosion Conference Series, 2006, 06125-0612514
- [24] R. Rufini, O. Di Pietro, A. Di Schino: Metals, Vol. 18, 2018, 519, DOI: 10.3390/met8070519

## LOCALISED CORROSION OF STAINLESS STEELS 316L AND 2205 IN SYNTHETIC BENTONITE PORE WATER AND BENTONITE SLURRY

Jan Stoulil<sup>1</sup>, Liudmila Pavlova<sup>1</sup>, Milan Kouřil<sup>1</sup> <sup>1)</sup> University of Chemistry and Technology Prague, Department of Metals and Corrosion Engineering

Received: 07.11.2018 Accepted: 10.01.2019

\*Corresponding author: jan.stoulil@vscht.cz; +420 22044 3750; University of Chemistry and Technology, Department of Metals and Corrosion Engineering, Technická 5, Prague 16628, Czech Republic

## Abstract

One concept for Czech canister construction for deep geological repository considers stainless steel as an inner case material. Corrosion resistance to localised (pitting/crevice) corrosion and stress corrosion cracking of austenitic stainless steel 316L and duplex steel 2205 was studied. The environment was synthetic bentonite pore water (SBPOW) of domestic bentonite BaM, or a slurry of bentonite in SBPOW. Tests were carried out between 40 °C and 90 °C under anaerobic conditions of a nitrogen atmosphere. The following methods were used for evaluation: potentiostatic tests at oxidation-reduction potential of the environment, long-term exposure tests in SBPOW and slurry, slow strain rate tensile test (SSRT), exposure test of U-bends, and optical microscopy. Results showed no susceptibility of either material to stress corrosion cracking. No localised corrosion was observed up to 70 °C. There was no localised attack observed in SBPOW at 90 °C, but there was localised corrosion detected in the bentonite slurry. Forced breakdown of the passive layer during SSRT, and artificial crevices (O-rings), showed no effect on localised corrosion propagation. The detrimental effect was probably a result of the adsorption ability of the bentonite particles, which allowed breakdown of passive layer and disabled repassivation of metastable pits.

**Keywords:** deep geological repository, stainless steel, bentonite, localised corrosion, stress corrosion cracking

### 1 Introduction

The Czech concept [1-8] of a HLW canister for deep geological repository considers three combinations of metallic material inner/outer case:

- stainless steel/carbon steel,
- carbon steel/copper,
- carbon steel/TiPd alloy.

In the first concept, a uniformly (predictable) corroding carbon steel case should overcome at least the aerobic period, when crevice corrosion would arise for sure on stainless steels. This work should verify what conditions in a repository could be acceptable for stainless steel. All oxygen is supposed to be consumed relatively fast in the repository, but the temperature could still be high, at 90 °C. The final temperature of the repository will be close to that of the host granitic rock. A conservative value is 40 °C, but the real temperature will probably be lower.

According to the mechanism of crevice corrosion, this kind of attack, based on differential aeration inside and outside the crevice is not very probable under anaerobic conditions. Pang and

Blackwood have published a study on Ti alloys, when anaerobic conditions led to activation [9], but this does not seem possible for stainless steel containing Cr and Ni. Stainless steels are susceptible to pitting corrosion in anaerobic conditions in the presence of sulphides. Superficial FeS working as cathode to the surrounding matrix is supposed to be responsible for the pitting [10, 11], but further studies have shown that there is inevitable oxidation of sulphide to thiosulphate by residual oxygen [12-14].

Stainless steel can be susceptible in repository environment under certain circumstances also to stress corrosion cracking [15, 16] or hydrogen embrittlement [17]. Stainless steel was considered also in USA [18] or Belgian [19] concept. When stainless steel is not attacked locally [20, 21], the corrosion rate in passivity seems reasonable for long term storage [22, 23].

The aim of this study is to verify the possibilities of crevice/pitting corrosion and stress corrosion cracking in anaerobic bentonite pore solution and bentonite slurry.

#### 2 Experimental

#### 2.1 Potentiostatic tests at ERED/OX

These experiments were carried out in an 800 ml beaker equipped with special PTFE cap for the working electrode (sample), counter electrode, reference electrode, thermometer, and nitrogen/air inlet. The beaker was heated on a plate controlled by a digital thermometer. All experiments were carried out at 90 °C in synthetic bentonite pore water (SBPOW), the composition of which is given in **Table 1**. SBPOW was estimated as equilibrium pore solution of saturated Czech domestic bentonite BaM with dry density 1600 kg.m<sup>-3</sup>. Samples were rods of stainless steel, 10 mm in diameter and 100 mm long. Materials used for these tests were austenitic stainless steel 316L and duplex stainless steel 2205. The chemical composition of both materials is given in **Table 2**. Samples were polished by emery paper P120 prior to all measurements.

Ion	Content (mol dm <sup>-3</sup> )
Na <sup>+</sup>	$1.88 \times 10^{-2}$
$\mathbf{K}^+$	$2.38 \times 10^{-3}$
$Ca^{2+}$	$3.49 \times 10^{-4}$
${ m Mg}^{2+}$	$1.11 \times 10^{-2}$
Cl	$7.88 \times 10^{-3}$
$SO_4^{2-}$	$1.21 \times 10^{-2}$
NO <sub>3</sub> -	$1.09 \times 10^{-2}$
HCO <sub>3</sub> -	$1.06 \times 10^{-3}$

Table 1 Chemical composition of synthetic bentonite pore water (SBPOW)

Samples were supplied with five O-rings at 10 mm spacing, working as artificial crevices. Those were placed in the lower part of the rod, because only 70 mm of the rods length was exposed to the solution. Platinum sheet (5 x 5 mm) served as counter electrode, and saturated silver-silver chloride electrode (ACLE) as reference. The reference electrode was placed in the salt bridge filled with SBPOW. Experiments were carried out in aerated and in deaerated conditions. The environment in the repository should be anaerobic; the experiments with aerated SBPOW were made to verify the influence of residual oxygen or of a technological defect from manufacturing when the inner case would be exposed to an aerated environment. The beaker was aerated for 1 h by air bubbling or deaerated by nitrogen, with simultaneous free corrosion potential ( $E_{CORR}$ )

settling. Potentiostatic polarisation at oxidation-reduction potential ( $E_{RED/OX}$ ) was started after that period.  $E_{RED/OX}$  was measured prior to these experiments and the average value was estimated to be 122 mV/ACLE for aerated SBPOW and -65 mV/ACLE for deaerated. The chloride content was increased approximately every 5 min by addition of concentrated solution of NaCl to 3, 10, 33 and 100-fold relative to the original value.

Sample	Mark	С	Si	Mn	Р	S	Cr	Ni	Mo
316L	А	0.021	0.25	1.88	0.044	0.028	16.70	10.60	2.11
2205	D	0.021	0.36	1.54	0.029	0.001	22.80	5.43	2.82

 Table 2 Chemical composition of materials (wt.%)

## 2.2 Exposure tests

These tests were carried out in special 1500 ml vessels with silicone sealing for prevention of oxygen access. Flasks were filled with SBPOW or bentonite slurry. The bentonite slurry was prepared 1:1 (w/w) with SBPOW to achieve equilibrium quickly. Rod samples with five O-rings were placed in vessels with SBPOW, while bare rods were placed in vessels with the slurry. Four austenitic and four duplex samples were exposed separately. Vessels were deaerated by nitrogen (99.99 %) in the glovebox for four days and exposed at 90 °C for six months and vessels at 40 °C for nine months.

Additionally were carried out experiments in order to estimate critical temperature for localised attack for both materials. This experiment was aggravated by addition of iron powder into the bentonite. The ratio of iron powder and bentonite was 1:3 (w/w). This dry mixture was mixed with SBPOW solution 1:1 (w/w) and left 1 week in ambient atmosphere to partially corrode the iron powder particles. Then was the vessel with slurry placed into the glovebox deaerated with nitrogen (99.99 %) for four days. After deaeration the samples were inserted into vessels and those were sealed. Vessels were exposed at 40, 50, 60 or 70 °C with duration of 6 months.

U-bend samples were also exposed. They were prepared from  $30 \times 130$  mm sheets, bent over a 20 mm spike and fixed with bolts. Thickness of the austenitic sheet was 3 mm and duplex steel 2 mm. Two U-bend samples of each material were exposed at 90 °C for four months after deaeration and sealing in glovebox as mentioned above.

## Slow strain rate tensile test

Rod samples were machined to reveal the working part in the middle of the rod (see **Fig. 1**). The working part was 4 mm in diameter and 10 mm long. Samples were subjected to slow strain rate tensile tests in SBPOW at 90 °C. Blank samples were exposed in demineralised water. The relative strain rate was  $1.32 \times 10^{-6} \text{ s}^{-1}$  (absolute 1.14 mm day<sup>-1</sup>). Samples were tested in SBPOW under different conditions: aerated/deaerated; increased chloride concentration 100-fold relative to original value; or a presence of heat flux. This was achieved by electrical heating using an external DC source. Input current was 2.7 A and voltage drop of 0.54 V at the working part was measured. Approximate heat flux from sample to solution was 11.6 kW m<sup>-2</sup>, which is 100-fold higher than a real canister heating in a repository.

2	3	4	5	6	7	8	9	10

Fig. 1 Sample for SSRT test of stress corrosion cracking

### 3 Results

## 3.1 Potentiostatic tests at ERED/OX

Curve records of both materials in deaerated SBPOW are given in **Fig. 2**. Both types of stainless steel remained passive when polarised to  $E_{RED/OX}$  of deaerated SBPOW, even in the case of 100-fold chloride content addition. The time of polarisation between each chloride addition was prolonged in one case, in order to observe the influence of time, but this prolongation did not lead to activation.

The same situation was observed for material 2205 under polarisation to  $E_{RED/OX}$  of aerated SBPOW (Fig. 3). In contrast, material 316L was activated in aerated environment in all measurements when 10-fold chloride content was added (Fig. 4).



**Fig. 2** Potentiostatic test in nitrogen-deaerated SBPOW at -65 mV/ACLE. Black curves - 2205; Grey curves - 316L. Dashed vertical lines show additions of chlorides



**Fig. 3** Potentiostatic test in aerated SBPOW at 122 mV/ACLE. Four samples of material 2205. Dashed vertical lines show additions of chlorides

DOI 10.12776/ams.v25i1.1197



Fig. 4 Potentiostatic test in aerated SBPOW at 122 mV/ACLE. Four samples of material 316L. Dashed vertical lines show additions of chlorides.

#### 3.2 Exposure tests

Long-term exposure with artificial crevices (O-rings) in deaerated SBPOW at 90 °C did not reveal any corrosion attack. Detail of the surface under the crevice-forming O-ring is shown in **Fig. 5**. The surface is clear, and non-shielded surfaces outside a crevice were covered by calcareous deposit formed from unstable SBPOW at high temperature.

All samples of both materials showed significant localised attack after the exposure in deaerated bentonite slurry at 90 °C (see **Fig. 6**). These pits are present on the entire surface of the samples. They do not show the classical shape of pitting corrosion; they are shallow and have open mouths, as can be seen on the cross-cut in **Fig. 7**. This type of localised attack (controlled by diffusion through salt cap over pit mouth) was published by Munoz and Schild [24] on material 309 in deaerated brines according to German repository concept.

A summary of mass loss evaluation is given in **Table 3**. Neither mass loss were estimated nor the localised attack was observed visually up to 70 °C in bentonite slurry even when contaminated by iron corrosion products, which could be in real conditions form carbon steel outer case. It seems that 70 °C is save temperature for both types of stainless steel for exposure in repository environment. Localised attack could arise at 90 °C in bentonite slurry as mentioned above. The mass loss was higher in material 2205, but the deviation was very high, thus there is not necessarily a significant difference between the materials. Despite the mass loss even in local area is not high, it is unacceptable for extreme canister lifetime.

Temperature (°C)	40		50	60	70	90		
Environment Material	SBPOW	BaM	BaM+Fe	BaM+Fe	BaM+Fe	BaM+Fe	SBPOW	BaM
316L	0	0	0	0	0	0	0	0.75±0.14
2205	0	0	0	0	0	0	0	$1.62 \pm 1.20$

 Table 3 Summary mass loss results (g.m<sup>-2</sup>.a<sup>-1</sup>) after 6 months exposure tests in bentonite-based environments

("SBPOW"-exposure in SBPOW with artificial crevices; "BaM"-slurry of bentonite BaM and SBPOW; "BaM+Fe"-slurry of bentonite BaM, iron powder and SBPOW)

U-bend samples were also attacked locally after exposure in bentonite slurry at 90 °C, but there was not observed localisation of the attack at the most strained sites of the bend. Pits were on the entire surface, similarly to the rod samples in the previous experiment. No corrosion cracks were observed on the bend surface.



**Fig. 5** Sample area of 2205 (D) rod, surrounding O-ring artificial crevice, after six-month exposure at 90 °C in nitrogen-deaerated SBPOW



**Fig. 6** Sample surface of 316L (A) rod after six-month exposure at 90 °C in nitrogen-deaerated bentonite slurry



Fig. 7 Detail cross-cut of a pit on the 316L (A) sample after six-month exposure at 90 °C in nitrogendeaerated bentonite slurry

### 3.3 Slow strain rate tensile test

A summary of all SSRT tests in deaerated SBPOW is given in **Fig. 8**. Despite the fact that the passive layer was mechanically forced to break down, no stress corrosion cracking was observed under any tested conditions. The environment was enriched in chloride content and heat flux was employed, but it did not lead to stress corrosion cracking. All samples showed only mechanical cracking with a typical 'neck' on the working part of the samples (see **Fig. 9**).



Fig. 8 Summary of stress–strain records of both materials – 2205 (D) and 316L (A) – obtained by SSRT test under different conditions

('DEMI'- test in 90 °C DEMI water; 'SBPOW' – test in aerated SBPOW; 'SBPOW + $N_2$ ' – test in deaerated SBPOW; 'SBPOW +Cl' – test in deaerated SBPOW with 100-fold increased content of chlorides; 'SBPOW +Cl+Q' – test in deaerated SBPOW with 100-fold increased content of chlorides and under heat flux)



Fig. 9 Example of a sample after SSRT test with typical 'neck' of mechanical fracture

## 4 Discussion

It was difficult to achieve corrosion activation of either material in SBPOW at 90 °C. Only an increase in chloride content with simultaneous action of artificial crevice and polarisation to  $E_{RED/OX}$  of an aerated solution allowed activation of austenitic stainless steel 316L. SSRT tests on both materials showed no effect of mechanical rupture of the passive layer in deaerated SBPOW, neither after a 100-fold increase in chloride content, nor in the presence of heat flux. Localised attack was observed in deaerated bentonite slurry at 90 °C. What was the most detrimental parameter of bentonite slurry in contrast to SBPOW? We can exclude crevice-forming particles of bentonite because artificial crevices (O-rings) did not show any effect in SBPOW. Also, mechanical rupture of the passive layer by solid bentonite particles can be discounted, because there was no effect of mechanical strain in the SSRT test, or in the exposure

of U-bend samples. Influence of additional dissolution of chlorides into the SBPOW at 90 °C can be also negotiated, since increase of chlorides up to 100-fold had no effect on formation of localised attack.

There are two most probable effects of solid bentonite on localised corrosion. The surface of bentonite particles is able to adsorb metal ions strongly. It is possible that the passive layer in contact with bentonite can be locally dissolved due to adsorption of metals from the passive layer onto bentonite. Moreover, the same adsorption makes the repassivation of the metastable pit formed more difficult. The open geometry of the pits is also an argument for the effect of bentonite adsorption.

The other effect is the possible presence of thiosulphates, which are well known to cause pitting corrosion of stainless steels. Thiosulphates in the environment are produced mostly by oxidation of sulphides. Sulphides are naturally contained in the bentonite (e.g. as pyrite) or they can be produced by sulphate-reducing bacteria. Microbial activity at 90 °C is less probable, but production of thiosulphates from natural bentonite sulphides cannot be excluded. Nevertheless, there were detected no thiosulphates in the solution after the exposure, thus if there any microbial activity proceeds, it changes the pore solution composition only locally.

#### 5 Conclusions

There was observed no localised corrosion or stress corrosion cracking at 90 °C in synthetic bentonite pore water. On the contrary, pitting corrosion at 90 °C in bentonite slurry was observed. This is attributed to the adsorption ability of bentonite particles. Both materials remained free of corrosion attack in deaerated bentonite slurry up to 70 °C.

#### References

- I. Pospiskova, et al.: Corrosion Engineering, Science and Technology, Vol. 52, 2017, No. S1, p. 6-10, DOI: 10.1080/1478422X.2017.1300379
- [2] J. Stoulil, V. Hemmer, V. Šefl, J. Bystrianský: Materials and Corrosion, Vol. 66, 2015, No. 4, p. 342-346, DOI: 10.1002/maco.201307468
- [3] J. Stoulil, J. Kaňok, M. Kouřil, H. Parschová, P. Novák: Journal of Nuclear Materials, Vol. 443, 2013, No. 1-3, p. 20-25, DOI: 10.1016/j.jnucmat.2013.06.031
- [4] J. Stoulil, et al.: Materials and Corrosion, Vol. 69, 2018, No. 9, p. 1163-1169, DOI: 10.1002/maco.201710014
- [5] D. Novikova, M. Kouřil, Š. Msallamová, J. Stoulil, N. Strnadová: Koroze a ochrana materialu, Vol. 60, 2016, No. 3, p. 68-73, DOI: 10.1515/kom-2016-0011
- [6] J. Stoulil, Y. R. Carreno, L. Pavlova, M. Kouřil, D. Dobrev: Koroze a ochrana materialu, Vol. 60, 2016, No. 5, p. 139-143, DOI: 10.1515/kom-2016-0022
- [7] J. Stoulil, D. Dobrev: Koroze a ochrana materialu, Vol. 60, 2016, No. 2, p. 60-67, DOI: 10.1515/kom-2016-0010
- [8] J. Stoulil, L. Horáčková, J. Říhová-Ambrožová: Koroze a ochrana materialu, Vol. 58, 2014, No. 2, p. 43-47, DOI: 10.2478/kom-2014-0006
- [9] J. Pang, D. J. Blackwood: Corrosion Science, Vol. 105, 2016, p. 17-24, DOI: 10.1016/j.corsci.2015.12.011
- [10] R. G. Bell, C. K. Lim: Canadian Journal of Microbiology, 1980, p. 242-245.
- [11] J. D. A. Miller: Microbial Aspects of Metallurgy, Springer, Netherlands, 1971.
- [12] A. M. Brennenstuhl, T. S. Gendron, R. Cleland: Corrosion Science, Vol. 35, 1993, No. 1-4, p. 699-711

- [13] R. C. Newman, W. P. Wong, A. Garner: Corrosion, Vol. 42, 1986, No. 8, p. 489-491
- [14] P. Perego, B. Fabiano, R. Pastorino, G. Randi: Bioprocess Engineering, Vol. 17, 1997, p. 103–109
- [15]C. Ornek: Performance Characterisation of Duplex Stainless Steel in Nuclear Waste Storage Environment, Dissertation Thesis, University of Manchester, 2015
- [16] [9.1.2019], K. Chiang and P. Shukla: https://www.nrc.gov/docs/ML1036/ML103620293.pdf
- [17] J. Stoulil et al.: Corrosion, Vol. 75, 2019, No. 4, p. 367-376, DOI: 10.5006/2852
- [18] R. B. Rebak: Selection of Corrosion Resistant Materials for Nuclear Waste Repositories, Report of Lawrence Livermore National Laboratory No. UCRL-PROC-221893, 2006
- [19]B. Kursten, et al.: Corrosion Engineering, Science and Technology, Vol. 46, 2011, No. 2, p. 91-97, DOI: 10.1179/1743278210Y.000000022
- [20] A. K. Roy, G. A. Henshall, R. D. McCright: *Electrochemical Corrosion Studies of Container Materials in Repository-Relevant Environments*, Report of U.S. Department of Energy Office of Scientific and Technical Information No. UCRL-ID-122860, 1995
- [21]X. He, D. S. Dunn, A. A. Csontos: Electrochimica Acta, Vol. 52, 2007, No. 27, p. 7556-7569, DOI: 10.1016/j.electacta.2006.12.077
- [22] X. He, T. Ahn, T. Sippel: Corrosion of borated stainless steel in water and humid air, Report of U.S. Nuclear Regulatory Commission No. NRC-02-07-006, 2011
- [23] T. Sakuragi, S. Yoshida, O. Kato, T. Tateishi: Progress in Nuclear Energy, Vol. 87, 2016, p. 26-31, DOI: 10.1016/j.pnucene.2015.10.008
- [24] A. G. Muñoz, D. Schild: Corrosion of austenitic steel in geochemical near-field conditions of high-level radioactive waste rock repositories, In: Proceedings of Eurocorr, Krakow (Poland), 2018

#### Acknowledgement

This work was supported by SÚRAO (Czech Radioactive Waste Repository Authority) under Project No. SO2013-088.

## VISCOSITY OF CuPb, CuPbSn, CuPbSnGa AND CuPbSnGaBi MELTS OF EQUIATOMIC COMPOSITIONS

Olga Chikova<sup>1)</sup>\*, Vladimir Tsepelev<sup>2)</sup>, Kseniya Shmakova<sup>3)</sup> Ural federal university, Yekaterinburg, Russia

Received: 01.12.2018 Accepted: 26.02.2019

\*Corresponding author:e-mail:chik63@mail.ru, Department of Physics, Ural federal university, Mira str., 19, Yekaterinburg, Russia

#### Abstract

We investigated the viscosity of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi melts of equiatomic compositions by the method of damped torsion vibrations of a crucible. We saw the melts of equiatomic composition as the melts high-entropy. All the investigated melts demonstrated the different temperature dependences of viscosity for heating and cooling. There is an anomalous reduction in viscosity resulted when the melt is heated to a specific temperature. The anomalous behaviour for viscosity we interpreted in terms of melt structure. This structural changes in the melt resulted when the melt is heated to a specific temperature. The microstructure of CuPbSnGaBi ingot of equiatomic composition we investigated using optical microscopy and measurement of microhardness. Collations data of the microstructures with of the microhardness gave three structural components: CuGa<sub>2</sub> dendrites,  $(Sn) + (Bi) + Bi_3Pb_7$  ternary eutectic and rounded Pb inclusions having dimensions of  $\approx 5 \mu m$ .

Keywords high-entropy melts, viscosity, Arrhenius law, microstructure of ingot, optical microscopy, microhardness

#### 1 Introduction

It is known that most multicomponent liquid alloys are far from ideal solutions and reveal a microinhomogeneous atomic distribution. Various experimental methods are used to study inhomogeneities. Models of the inhomogeneous structure of liquid alloys have been developed [1-10]. The existence of inhomogeneous structure in liquid alloys within some temperature range is related to the anomalous temperature dependences of physicochemical properties. For example there are the anomalies of the temperature dependence of the viscosity within some temperature range after melting [1, 2, 6, 7]. However, literature data for multicomponent melts are scarce.

The results of viscosity measurements of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi equiatomic composition melts are presented in this work. We consider multicomponent melts as high-entropy melts. We discussed the laws of the existence of a microinhomogeneous distribution of atoms for a new group of multicomponent liquid alloys–high-entropy alloys (HEA) [11–15]. For destruction of microinhomogeneity in liquid alloy involves it heating to a temperature at which complete mixing of components and formation of a homogeneous solution come about, which substantially changes conditions of metal crystallization. It is known such this heating of liquid alloy at subsequent cooling and crystallization, even at relatively low cooling rates (1-10 K/s) enables getting a microstructure similar to microstructure, which is formed at high cooling rates [6]. The purpose of this study was to determine the temperature of

heating, leads to the destruction of microinhomogeneities in the melts of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi equiatomic composition.

Current interest in studying of conditions of crystallization of high-entropy melts is increasing.. The high entropy of mixing stabilizes the formation of solid solutions and prevents the formation of intermetallic phases during solidification. High-entropy alloys possess high strength and thermal stability, combined with good resistance to oxidation and corrosion. An important factor in obtaining high-entropy alloys is high cooling rate of metal during crystallization, which makes it impossible to disintegrate of solid solution and formation of chemical compounds. High metal cooling rate, which is technically difficult to ensure, can be replaced by a destruction of the microinhomogeneity of chemical composition of liquid alloy before crystallization.

The high-entropy alloys can have either high strength or high ductility, and simultaneous achievement of both still constitutes a tough challenge. The inferior castability and the compositional segregation of high-entropy alloys are also obstacles for their technological applications. To tackle these problems for alloy CuPbSnGaBi, here we proposed a novel strategy to design high-entropy alloys using the eutectic alloy concept, i.e. to achieve a microstructure composed of alternating soft and hard phases. As a manifestation of this concept, a before AlCoCrFeNi eutectic high-entropy alloy was designed [16]. This high-entropy alloy possessed a fine lamellar microstructure, and showed an unprecedented combination of high tensile and high fracture strength at room temperature.

The present study investigates the viscosity of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi equiatomic composition liquid alloys, with special attention given to the analysis of the temperature dependence of the viscosity coefficient using the theory of absolute reaction rates. The microstructure of the obtained sample CuPbSnGaBi of equiatomic composition after the viscosity measurement were researched additionally by means of optical microscopy and measurement of microhardness.

#### 2 Experimental material(s) and methods

The sample alloys of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi equiatomic composition were produced in the laboratory in a resistance furnace in an inert gas atmosphere. The starting materials were Mk00 copper, tin brand "000", lead brand "h", bismuth granular mark "h", gallium brand "0" and bismuth mark "h" ingots. The kinematic viscosity was measured using the oscillating cylinder method during heating and subsequent cooling. The measurements were carried out in the temperature range 600–1600 K with the isothermal delay no less than 30 min at relatively small (50 K) stepwise temperature changes. A given temperature was maintained to accuracy to 1 K using a high-precision controller. The vibration parameters were measured using an optical method with a system of photoregistration of vibrations. The experimental technique and the processing of experimental data have been described in detail [17, 18]. BeO crucibles were used in all experiments. All of the experiments were carried out in a high-purity helium atmosphere at a pressure of 10<sup>5</sup> Pa. The systematic error of measuring viscosity was 3wt% and including the random error no higher than 1.5% at a confidence level of 95%.

Metallographic investigation of the structure of the CuPbSnGaBi sample of the equiatomic composition was carried out using conventional methods. The cooling rate during the crystallization of the sample was 10 K/s. The study was conducted by means of optical on unetched and polished sections of etched alloy (etching carried out in an alcoholic solution of 3% HNO<sub>3</sub>). A microhardness gage PMT-3 was used for the measurement of microhardness with a load of 0.1–0.5 H.

#### 3 Results and discussion

**Fig. 1** and **Table 2** show the results of a viscometric study of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi liquid alloys of equiatomic composition. All of the investigated melts demonstrate different heating and cooling temperature dependences of viscosity v(T), i.e. hysteresis. The  $T^*$  temperature was measured by following the experience of the authors [8, 9, 10].  $T^*$  is the temperature of the beginning of the matching portion of the temperature dependence of the viscosity, which is obtained by heating and cooling. Temperature  $T^*$  is 1410 K for alloy CuPbSnGaBi. Notice that there is a higher viscosity measured on heating than on cooling (**Fig. 1**). The most significant decrease in the viscosity at low temperatures (near the liquidus) is for melt CuPbSn. The temperature  $T^*$  value is increased with increasing number of components in the melt (**Table** 

1). It is interesting to note that values of  $\frac{dv}{dT}$  for all studied melts during cooling were equal to

or lower than the corresponding values of  $\frac{dv}{dT}$  recorded during heating (Fig. 1). Heating the

liquid alloys CuPbSnGa and CuPbSnGaBi to 1100 K leads to an increase in the viscosity. The increase in the viscosity on heating can be explained by the quasi-gaseous state in the melt, which is retained during subsequent cooling of the metallic liquid. The quasi-gaseous behaviour of the melt, i.e. an increase in the viscosity with the temperature of the metallic liquid was earlier noted in Ref. 2 for the liquid metal and was associated with changes in the vacancy subsystem of the melt.



Fig. 1 Viscosity of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi melts of equiatomic compositions [8,9,10]

Our attention was focused on the changing characteristics of the viscous flow of the melts. The activation energy of viscous flow and the entropy factor in the Arrhenius equation  $v = A \exp(\frac{E}{RT})$  change when heating the liquid alloy to the temperature  $T^{\#}$  ( $T^{\#}$ - is temperature of the beginning of structural transformations). The temperature dependences of viscosity of liquid CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi alloys of equiatomic compositions and deviation from the Arrhenius behaviour were found when the temperature was about 100–300 K higher than the melting point (**Fig. 2**).



**Fig. 2** The dependence of  $\ln v$  on (1000/T) for melts upon cooling

The abnormal increasing of the viscosity and activation energy indicate changes of the melt structure during cooling. The temperature  $T^{\#}$  for CuPb; CuPbSn; CuPbSnGa and CuPbSnGaBi melts is in the range of 900–1180 K. With increasing number of components in the melt, the value of  $T^{\#}$  is reduced (**Table 1**).

Table 1	The temperature of anomalous behaviour for viscosity of the melt, which is interpreted
	in terms of the characteristics of the structural state melts

The alloy of equiatomic compositions	<i>T</i> *, K	<i>T</i> <sup>#</sup> , K		
CuPb	1410	-		
CuPbSn	1180	1180		
CuPbSnGa	1230	1060		
CuPbSnGaBi	1460	920		

The temperature dependence of the viscosity coefficient deviates from predictions of the classical theory of absolute reaction rates. According to the theory of absolute reaction rates [19], melt viscosity can be described by the

equation 
$$\nu = \frac{hN_{\rm A}}{\mu} \exp\left(\Delta G^{\#}/RT\right) = \frac{hN_{\rm A}}{\mu} \exp\left(-\frac{\Delta S^{\#}}{R}\right) \exp\left(\frac{\Delta H^{\#}}{RT}\right)$$

where *h* is the Planck constant,  $N_A$  is the Avogadro constant,  $\Delta G^{\#}$  is the free energy of activation of viscous flow,  $\mu$  is the molar mass,  $\Delta H^{\#}$  is the enthalpy of activation of viscous flow,  $\Delta S^{\#}$  is the entropy of activation of viscous flow, *R* is the universal gas constant and *T* is the temperature.

The entropy factor in the Arrhenius equation  $A = \frac{hN_A}{\mu} \exp(-\frac{\Delta S^{\#}}{R})$  depends on the entropy

of viscous flow,  $\Delta S^{\#}$ . The activation energy  $\varepsilon$  and the entropy of activation of viscous flow  $\Delta S^{\#}$  for CuPbSn, CuPbSnGa and CuPbSnGaBi melts upon cooling were calculated (**Table 2**). With an increasing number of components in the melt, the absolute values of the activation energy  $\varepsilon$  and entropy of activation of viscous flow  $\Delta S^{\#}$  are reduced.

**Table 2** The activation energy  $\varepsilon$  and entropy of activation of viscous flow  $\Delta S^{\#}$  for melts upon cooling

Alloy	$-\Delta S^{\#}, J \cdot K^{-1}$	Activation energy $\varepsilon$ , kJ·mol <sup>-1</sup>
CuPb	31.3	14.9
CuPbSn	29.7	13.5
CuPbSnGa	28.8	12.5
CuPbSnGaBi	27.6	9.97

In experiments with liquid alloy CuPb, lower viscosity values than those specified in previous reports [20-22] were recorded, which the authors attribute to the equiatomic alloy composition (up to 0.01 g). The prevailing feature of the liquid Cu50Pb50 system is the existence of a monotectic turning.

The of viscosity results for alloys CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi equiatomic composition can be qualitatively interpreted using the concepts of microheterogeneity in liquid alloys [8, 9]. According to these concepts, when the liquidus line is reached, an atomically homogeneous solution does not form immediately and the heterogeneity state of the melt in the form of two phases differing in chemical composition is retained in the temperature range characteristic of each composition. In the region of states where a liquid metal contains microheterogeneities, the values of viscosity measured on heating and cooling a sample are different. At higher temperatures, the difference in the values of viscosity is within the random measurement error. The temperature  $T^*$  corresponding to branching curves v(T) corresponds to the transition of the melt to the state of true solution. The increase in the melt viscosity during heating in microinhomogeneous condition can be explained by the process of dispersing the microheterogeneities. The temperature  $T^{\#}$  corresponds to the beginning of the process of destroying microheterogeneities. Experiments in Ref. 6 show that for the destruction of microscopic inhomogeneities, enough liquid alloys needs to be heated to  $T^{\#}$  and to stand for a while. The value  $T^{\#}$  is always less than or equal to  $T^{*}$ . Differences between  $T^{\#}$  and  $T^{*}$  values were detected for the alloys composed of four and five components (Table 2).

The main problem of production of the HEAs is related to the formation of a homogeneous structure of volumetric ingots. A separation by density in the gravitational field occurs on

cooling of the multicomponent liquid alloys. The result is a heterogeneous ingot, the lower portion of which is enriched by the heavy components during curing. The separation of solidifying liquid metal can be suppressed by using a high cooling rate  $(10^3-10^6 \text{ K/s})$ . The most promising method of suppressing the separation of HEAs and the production of a material with a homogeneous structure is a homogenization of metallic liquid, i.e. overheating above the certain temperature  $T^*$  [6]. This method makes it possible to produce bulk ingots with the required structure under conditions of natural gravitation even at fairly low cooling rates. After such an overheating, the melt changes irreversibly to the state of true solution, which substantially changes the conditions of metal solidification. We have the assumption that the heating of the liquid metal above the temperature  $T^*$  in the subsequent crystallization even at relatively low speeds will provide homogeneous structure volumetric ingots for the HEAs [14].

To test this hypothesis, we conducted a metallographic study of the structure of the ingot CuPbSnGaBi alloy obtained after the viscosity measurement. Before crystallization, the ingot was heated to a temperature higher than  $T^*$ .

Images of the microstructure of CuPbSnGaBi sample of equiatomic alloy are shown in **Fig. 3**. The microstructure consists of multiple phases evenly spread over the section of the ingot.



Fig. 3 The microstructure of the CuPbSnGaBi alloy [9]

After chemical etching, optical microscopy can distinguish the phase of the dendrites' origin, the dark phase of the small discharge and the interdendritic space consisting of plates, reflecting the morphology of the eutectic plate. The nature of the different phases also proves the sharp difference in the hardness of the structural components. The microhardness of the dendrites is about 2400 MPa, of the dark secretions is 180 MPa and for the eutectic phase is 150 MPa. The authors have suggested according to the data in Ref. 19, that the dendrites are CuGa<sub>2</sub>. The data of the ternary eutectic (Sn) + (Bi) + Bi<sub>3</sub>Pb<sub>7</sub> obtained from metallographic analysis and measurement of the microhardness also agree with the data in Ref. 20. The third component of the structure of the sample is clearly distinguished rounded inclusions of Pb having dimensions of  $\approx 5 \,\mu\text{m}$ .

#### 4 Conclusion

1. A viscometric studies of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi melts of equiatomic composition by heating and subsequent cooling were performed. Viscosity was measured using damping torsional vibrations of a crucible with a melt in the temperature range 600–1600 K.
- 2. The polythermals of the viscosity measured during heating and cooling are different from each other. For all alloys, we have identified specific temperatures at which an irreversible structural change in the state of the melt occurs:  $T^*$  and  $T^{\#}$ . The temperature  $T^*$  at the beginning of the matching portion of the temperature dependence of the viscosity, which is obtained by heating and cooling, was measured. The value of the temperature  $T^*$  is in the range 1180–1460 K. When heated to  $T^{\#}$ , the melts have a sharp change in the characteristics of viscous flow; the activation energy of viscous flow and the entropy factor in the Arrhenius equation are changed. The value of  $T^{\#}$  is in the range 900–950 K.
- 3. For all of the studied melts, the values of viscosity during cooling were equal to or lower than the corresponding values recorded during heating. The most significant decrease in the melt viscosity near the liquidus temperature was for the melt CuPbSn.
- 4. A metallographic study of the structure of the ingot CuPbSnGaBi alloy obtained after the viscosity measurement was conducted. The microstructure consists of multiple phases evenly spread over the section of the ingot. The measurement of microhardness, showed CuGa<sub>2</sub> dendrites, a (Sn) + (Bi) + Bi<sub>3</sub>Pb<sub>7</sub> triple eutectic, and Pb round inclusions, measuring about 5 microns. We showed that if the liquid metal is heated above the temperature  $T^*$ , then the subsequent crystallization even at relatively low speeds will provide homogeneous structure volumetric ingots for the high-entropy CuPbSnGaBi alloy.
- 5. The results of the viscosity of CuPb, CuPbSn, CuPbSnGa and CuPbSnGaBi melts of equiatomic composition study can be qualitatively interpreted using the concepts of microheterogeneity in liquid alloys. The temperature  $T^*$  corresponding to branching curves v(T) corresponds to the transition of the melt to the state of the true solution. The increase in the melt viscosity during heating in a microinhomogeneous condition can be explained by the process of dispersing microheterogeneities. The temperature  $T^*$  corresponds to the beginning of the process of destruction of microheterogeneities.

## References

- A. Yakymovych, V. Sklyarchuk, Yu. Plevachuk, S. Mudry: Reviews on Advanced Materials Science, Vol. 23, 2010, No. 2, p. 213-217
- [2] A. Bel'tyukov, S. Menshikova, V. Lad'yanov: Journal of Non-Crystalline Solids, Vol. 410, 2015, p. 1-6, DOI: 10.1016/j.jnoncrysol.2014.11.028
- [3] P. Popel, M. Calvo-Dahlborg, U. Dahlborg: Journal of Non-Crystalline Solids, Vol. 353, 2007, No. 32-40, p. 3243-3253, DOI: 10.1016/j.jnoncrysol.2007.05.179
- [4] Yu. Plevachuk, V. Sklyarchuk, A. Yakymovych, G. Gerbeth : Journal of Non-Crystalline Solids, Vol. 354, 2008, p. 4443-4447, DOI: 10.1016/j.jnoncrysol.2008.06.068
- [5] M. Li, Y. Zhang, C. Wu, H. Geng: Journal of Non-Crystalline Solids, Vol. 122, No. 3, 2016, p. 171, DOI: 10.1007/s00339-016-9723-5
- [6] P.S. Popel, O.A. Chikova, V.M. Matveev: High Temperature Materials and Processes Vol. 14, No. 4, 1995, p. 219-233, DOI: 10.1515/HTMP.1995.14.4.219
- [7] S. Mudry, A. Korolyshyn, V. Vus, A. Yakymovych: Journal of Molecular Liquids, Vol. 179, 2013. p. 94-97, DOI: 10.1016/j.molliq.2012.12.019
- [8] O. Chikova, V. Tsepelev, V. V'yukhin: Russian Journal of Non-Ferrous Metals, Vol. 56, 2015, No. 3, p. 246–250, DOI: 10.3103/S1067821215030037

- [9] O. Chikova, V. Tsepelev, V. V'yukhin, K. Shmakova: Metallurgist, Vol. 59, 2015, No. 5–6, p. 435-440, DOI: 10.1007/s11015-0123-4
- [10] V.V. V'yukhin, V. S. Tsepelev, O. A. Chikova, A. M. Sokolov: Russian metallurgy (Metally), 2015, No. 7, p. 525-528, DOI: 10.1134/S0036029515070137
- [11] Jien-Wei Yeh High-entropy multielement alloys: US Patent US 20020159914, 31 October 2002.
- [12] T. Chung-Jin, et al: Metallurgical and Materials Trasactions A, 36A, 2005, No. 4, p. 881-893, DOI: 10.1007/s11661-005-0283-0
- [13] N. Kourov et al: Journal of Alloys and Compounds, 2015, No. 636 p. 304-309, DOI: 10.1016/j.jallcom.2014.12.012
- [14] P. Jablonski, J. Licavoli, M. Gao, J. Hawk: JOM, Vol. 67, 2015, No. 10, p. 2278-2287, DOI: 10.1007/s11837-015-1540-3
- [15] B. Cantor, T. Chang, P. Knight, A. Vincent: Materials science and engineering A-Structural materials properties microstructure and processing, 2004, No. 375-377, SI, p. 213-218, DOI: 10.1016/j.msea.2003.10.257
- [16] Y. Lu et al.: Eutectic High-Entropy Alloys, Scientific reports, Vol. 4, 2014, 6200, DOI: 10.1038/srep06200
- [17] V. Konashkov, V. Tsepelev, V. V'Yukhin, A. Povodator, A. Podol'skaya Instruments and Experimental Techniques, Vol. 54, 2011, No. 2, p. 284-285, DOI: 10.1134/S0020441211020187
- [18] A. Povodator, V. Tsepelev, V. Konashkov: Steel in Translation, Vol. 45, 2015, No. 6, p. 407-411, DOI: 10.3103/S096709121506011X
- [19] S. Glasstone, K.J. Laidler, H. Eyring: *The theory of rate processes*: first ed, New York, Princeton University 1941, 611
- [20] L. Gvozdeva, A. Lyubimov : Ukrainian Physics Journal, 1967, No. 12, p. 208-213
- [21]F. Silze et al: Materials and Design, Vol. 91, 2016, p. 11-18, DOI: 10.1016/j.matdes.2015.11.034
- [22] K. Moon, W. Boettinger, U. Kattner, C. Handwerker, D. Lee: Journal of Electronic Materials, Vol. 30, 2001, No. 1, p. 45-52, DOI: 10.1007/s11664-001-0213-x

#### Acknowledgement

Authors are grateful for the support of experimental works by Act 211 Government Russian Federation, contract  $N \ge 02.A03.21.0006$ .

# PREPARATION OF Cu MATRIX COMPOSITE REINFORCED WITH IN-SITU NANOSIZED Al<sub>2</sub>O<sub>3</sub> PARTICLE POWDER FROM METAL NITRATES

Hai Minh Le<sup>1</sup>, Yen Ngoc Nguyen<sup>1</sup>, Duong Tien Hoang Truong<sup>1</sup>, Huy Duc Vu<sup>1</sup>, Hai Hong Nguyen<sup>1</sup>, Khanh Quoc Dang<sup>1</sup>\*

<sup>1)</sup> School of Materials Science and Engineering, Hanoi University of Science and Technology, Hanoi, Vietnam

Received: 04.01.2019 Accepted: 28.02.2019

\*Corresponding author: e-mail: khanh.dangquoc@hust.edu.vn, Tel.: +84 24 3868 0355, School of Materials Science and Engineering, Hanoi University of Science and Technology, No.1, Dai Co Viet Street, Hai Ba Trung, Hanoi, Vietnam

# Abstract

The objective of the present work is to investigate the feasibility of the synthesis of copper matrix composite reinforced with in-situ nanosized Al<sub>2</sub>O<sub>3</sub> particle powder via combustion synthesis method from metal nitrates followed by reducing process at high temperature. The starting nitrates Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O composition corresponds to Cu-30%Al<sub>2</sub>O<sub>3</sub>. X-ray Diffraction (XRD) patterns of the obtained powders indicated the presence of the oxides CuO and CuAl<sub>2</sub>O<sub>4</sub>. The powder had the size of 75 ± 10 nm after deagglomerating by soft ball milling for 24h. After reducing in CO at 1000°C for 3h, the peaks of the oxides were no longer observed and were replaced by the peaks of Cu and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The morphology of the reduced powders observed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analysis showed well distribution of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles within the Cu matrix with an average particle size of 40 nm.

Keywords: Cu-Al<sub>2</sub>O<sub>3</sub> nanocomposite, CuAl<sub>2</sub>O<sub>4</sub>, CuAlO<sub>2</sub>, combustion synthesis, reduction

# 1 Introduction

The aim of fabricating copper-based composites reinforced with dispersed ceramic particles is to enhance the mechanical properties of copper, in particular their higher specific strength and good elevated temperature mechanical properties while still maintaining the high electrical and thermal conductivities [1-8]. Currently, there are two main routes of producing such kind of composites, which are ex-situ and in-situ processes. In in-situ synthesis technique, the reinforcing ceramic phases are synthesized in the metallic matrix by a chemical reaction during the composite fabrication. Consequently, compared to ex-situ synthesis technique, in-situ routes introduce significant advantages such as nanosize, good distribution and thermodynamical stability of reinforcing particulate phases [9-13], which considerably enhance the properties of the composites.

The Cu nanocomposite reinforced by in-situ Al<sub>2</sub>O<sub>3</sub> have been developed through different synthesis routes such as mechanical alloying and rapid solidification. Ying and Zhang studied the synthesis of a Cu-20 vol.% Al<sub>2</sub>O<sub>3</sub> nanocomposite via mechanical milling of a Cu-Al powder together with CuO powder [14]. Al<sub>2</sub>O<sub>3</sub> particles in the consolidated composite material have a size smaller than 200 nm in diameter. Recently, chemical route has emerged as a newly developed method to prepare Cu nanocomposites reinforced with nanosized Al<sub>2</sub>O<sub>3</sub> particles. Cu

nanocomposites reinforced by 5, 10, and 15 wt.% Al<sub>2</sub>O<sub>3</sub> were prepared using mechano-chemical method [15-18]. This research reported that Cu was added to aqueous solution of aluminum nitrate or aqueous solution of aluminum nitrate and ammonium hydroxide. The average particle size of Cu and Al<sub>2</sub>O<sub>3</sub> were 209 nm and 50 nm, respectively. Krakum et al. prepared Cu-Al<sub>2</sub>O<sub>3</sub> composite via directly mixing of CuO and Al<sub>2</sub>O<sub>3</sub> powders [19]. The powder mixture was then ball-milled in ethanol and sintered in an SPS apparatus to achieve highly dense CuAlO<sub>2</sub> sample. This bulk sample was then reduced by H<sub>2</sub> gas to obtain Cu-Al<sub>2</sub>O<sub>3</sub> composite.

A new process to produce homogeneous Cu-Al<sub>2</sub>O<sub>3</sub> nanocomposites from combustion reaction of metal nitrates was developed in the present study. The final Cu-Al<sub>2</sub>O<sub>3</sub> nanocomposites was obtained by CO reducing and sintering process. The phases present, morphology and microstructure will be determined by X-ray Diffraction (XRD), Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy analysis (EDS) techniques.

#### 2 Experimental procedure

Copper nitrate  $Cu(NO_3)_2.3H_2O$  (>99%) and aluminum nitrate  $(Al(NO_3)_3.9H_2O$  (>99%) as oxidizers and urea  $CH_4N_2O$  (>99%), as fuel were used to produce Cu-30 vol%  $Al_2O_3$  nanocomposite, purchased from Xilong Scientific Co. Ltd., China. Precursor materials were mixed by a fixed ratio, and then dissolved in distilled water. Subsequently, the solution was placed in an electric resistance furnace (Linn HT1300, Germany) which was preheated at 500°C. The combustion reaction was performed according to the reactions (1) and (2).

$$3Cu(NO_{3})_{2}(aq) + 6Al(NO_{3})_{3}(aq) + 20CH_{4}N_{2}O(aq) \rightarrow 3CuAl_{2}O_{4}(s) + 20CO_{2}(g) + 40H_{2}O(g) + 32N_{2}(g)$$
(1.)

$$3Cu(NO_{3})_{2}(aq) + 5CH_{4}N_{2}O(aq) \rightarrow 3CuO(s) + 5CO_{2}(g) + 10H_{2}O(g) + 8N_{2}(g)$$
(2.)

The synthesized product was milled for 24 hours in a pure ethanol solution (96%) using alumina balls with ball-to-powder mass ratio of 20/1 then dried at 120°C for 24 hours and calcined at 1100°C for 2 hours. The reduction process was carried out at 1000°C for 3 hours by annealing in a forming gas (99.97% CO) environment. The green compacts were formed by uniaxial pressing in a 10 mm inner diameter cylindrical steel die under a uniaxial applied pressure of 500 MPa. The compacted samples were then sintered by a tube furnace (Linn HT1200, Germany) at 1000°C for 3 hours with a heating rate of 5°C/min in argon atmosphere.

The phase analysis was carried out by XRD (D5000 Siemens, Germany) using Cu K $\alpha$  radiation. The morphology of the synthesized powders and the sintered samples was characterized by a fieldemitting scanning electron microscope (FE-SEM Hitachi S4800, Japan). The particle size and the size distribution were evaluated by ImageJ software through SEM images. In addition, EDS was performed to identify the elements that present in the synthesized powders.

#### **3** Results and Discussion





Fig. 1 The XRD patterns of (a) the combustion-synthesized powder, (b) after annealed at 1100°C in air for 2 hours and (c) after reduction in CO at 1000°C for 3 hours



**Fig. 2** SEM images of combustion-synthesized powder annealed at 1100°C in air for 2 hours in (a) SE mode, (b) BSE mode and its corresponding EDS patterns acquired on (c) A and (d) B areas

The evolution of the microstructure organization of the combustion-synthesized powder according to each step of the thermal treatment process can be deduced from XRD spectra (**Fig. 1**). The XRD spectrum of the combustion-synthesized powder exhibited almost all the main CuO and CuAl<sub>2</sub>O<sub>4</sub>

reflections (**Fig. 1a**). The appeared peaks were very broad indicating the poor crystalline nature of combustion synthesized product due to nanosized effect. After 2-hour annealing at 1100°C in air, the peaks of CuO phase was more intense and well-defined indicating a good crystallinity of the annealed product. However, the CuAl<sub>2</sub>O<sub>4</sub> peaks disappeared and replaced by the peaks of CuAlO<sub>2</sub> (**Fig. 1b**). According to Hu et al., [20] the decomposition of CuAl<sub>2</sub>O<sub>4</sub> at a temperature higher than 900°C led to the formation of CuAlO<sub>2</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phases depending on the partial pressure of O<sub>2</sub>. However, if the amount of CuO is excessive, the solid–solid reaction between CuO and CuAl<sub>2</sub>O<sub>4</sub> can take place to form CuAlO<sub>2</sub>. The XRD pattern of annealed powder after reduction in the presence of reducing gas CO at 1000°C for 3 hours showed the sharp and high intense peaks of metallic Cu (**Fig. 1c**). The small peak width indicated a good crystallinity with a large grain size of the formed Cu. However, no peaks of Al<sub>2</sub>O<sub>3</sub> phase was observed in XRD spectrum. The invisibility of Al<sub>2</sub>O<sub>3</sub> could be due to several reasons including poor crystallinity and small particle size of the generated Al<sub>2</sub>O<sub>3</sub> and its much lower backscattering factor compared to Cu.

The SEM image in secondary electron mode of the combustion-synthesized powder after annealing was displayed in **Fig. 2** showing a monomodal particle size distribution with an average size of 100 nm. Back-scattered SEM images of the annealed powder illustrated the contrast between CuO and CuAlO<sub>2</sub> (**Fig. 2b**). EDS analysis (**Fig. 2c,d**) indicates that the bright area (marked as A) and the dark area (marked as B) are CuAlO<sub>2</sub> and CuO, respectively.



**Fig. 3** SEM images of the composite powder reduced by CO at 1000°C for 3 hours in (a) powder, (b) its polished surface and corresponding EDS patterns acquired on (c) dark and (d) white areas

The reduction in the presence of reducing gas CO at 1000°C for 3 hours led to the formation of pores, which were uniformly distributed along the grain surfaces (**Fig. 3a**). In order to investigate

the distribution homogeneity of reinforcing particulates, back-scattered SEM (mode) and corresponding EDS of the composite powder are presented in **Fig. 3b–d**. The EDS spectra which acquired on the dark (**Fig. 3d**) and white (**Fig. 3c**) regions clearly demonstrated the existences of Cu matrix and Al<sub>2</sub>O<sub>3</sub> particulate reinforcement. In the composites, the in-situ Al<sub>2</sub>O<sub>3</sub> particles with an average size of 70 nm were uniformly dispersed throughout in the Cu matrix, as seen in **Fig. 3b**.



Fig. 4 XRD patterns of the Cu-30 vol% Al<sub>2</sub>O<sub>3</sub> composite sintered at 1000°C for 3 hours



**Fig. 5** The SEM images of the sintered composite in (a) SE mode, (b) BSE mode from the same area and its corresponding EDS patterns acquired on (c) bright and (d) dark areas

The XRD pattern of the sintered Cu-30 vol%  $Al_2O_3$  composite is plotted on a logarithmic scale (Fig. 4) in order to observe the low-intense peaks. Apart from the peaks of copper matrix, the

XRD pattern shows the reflections corresponding to the hexagonal close-packed structure of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. However, these Al<sub>2</sub>O<sub>3</sub> peaks were not observed after reducing in CO. Their appearance could be due to that the heat treatment recovered considerably internal strains and made the crystallite size increase remarkably. SEM images of the sintered composite in both (a) secondary electron and (b) back-scattered electron modes from the same area and their corresponding EDS patterns acquired on (c) bright and (d) dark areas (**Fig. 5a-d**) proved a nanosized and well-dispered Al<sub>2</sub>O<sub>3</sub> particles within Cu matrix. The average size of the in-situ reinforced Al<sub>2</sub>O<sub>3</sub> particles was about 40 nm. In the future works, the fabrication of bulk nanocomposite with different reinforcement composition and their mechanical and physical properties will be studied.

#### 4 Conclusions

Cu-30vol.% Al<sub>2</sub>O<sub>3</sub> nanocomposites have been successfully synthesized by chemical routes through combustion reaction of metal nitrates (i.e. Al(NO<sub>3</sub>)<sub>3</sub> and Cu(NO<sub>3</sub>)<sub>2</sub>) followed by CO reduction and sintering. The obtained XRD spectra revealed that the mixture of CuO and CuAl<sub>2</sub>O<sub>4</sub> powder formed after combustion reaction was transferred to CuO and CuAlO<sub>2</sub> after annealing and to composite powder of Cu/Al<sub>2</sub>O<sub>3</sub> after reducing by CO. SEM images in both SE and BSE mode and its corresponding EDS patterns showed nanosized and well-dispered of Al<sub>2</sub>O<sub>3</sub> particles within Cu matrix. The average size of the in-situ reinforced Al<sub>2</sub>O<sub>3</sub> particles was 40 nm.

#### References

- S. Sheibani, M. Khakbiz, M. Omidi: Journal of Alloys and Compounds, Vol. 477, 2009, No. 1-2, p. 683-687, DOI: 10.1016/j.jallcom.2008.10.095
- [2] C. Biseli, D. G. Morris, N. Randall: Scripta Metallurgica et Materialia, Vol. 30, 1994, No. 10, p. 1327-1332, DOI: 10.1016/0956-716X(94)90267-4
- [3] T. Takahashi, Y. Hashimoto: Materials Transactions JIM, Vol. 32, 1991, No. 4, p. 389-397, DOI: 10.2320/matertrans1989.32.389
- [4] M. T. Marques, V. Livramento, J. B. Correia, A. Almeida, R. Vilar: Materials Science and Engineering A, Vol. 399, 2005, No. 1-2, p. 382-386, DOI: 10.1016/j.msea.2005.03.090
- [5] M. T. Marques, V. Livramento, J. B. Correia, A. Almeida, R. Vilar: Journal of Alloys and Compounds, Vol. 434-435, 2007, p. 481-484, DOI: 10.1016/j.jallcom.2006.08.307
- [6] Z. Hussain, R. Othman, B. D. Long, U. Minoru: Journal of Alloys and Compounds, Vol. 464, 2008, No. 1-2, p. 185-189, DOI: 10.1016/j.jallcom.2007.10.026
- [7] H. Zuhailawati, T. L. Yong: Materials Science and Engineering A, Vol. 505, 2009, No. 1-2, p. 27-30, DOI: 10.1016/j.msea.2008.10.038
- [8] E. Botcharova et al.: Journal of Alloys and Compounds, Vol. 351, 2003, No. 1-2, p. 119-125, DOI: 10.1016/S0925-8388(02)01025-3
- [9] L. Froyen, J. D. Wilde: Materials Science Forum, Vol. 437-438, 2003, p. 141-144, DOI: 10.4028
- [10] T. Wang et al.: Materials & Design, Vol. 65, 2015, p. 280-288, DOI: 10.1016/j.matdes.2014.09.025
- [11] J. Ružić, J. Stašić, V. Rajković, D. Božić: Materials & Design, Vol. 62, 2014, p. 409-415, DOI: 10.1016/j.matdes.2014.05.036
- [12] N. Soltani et al.: Materials & Design, Vol. 53, 2014, p. 774-781, DOI: 10.1016/j.matdes.2013.07.084
- [13] S. C Tjong, Z. Y Ma: Materials Science and Engineering: R: Reports, Vol. 29, 2000, Issues 3-4, p. 49-113, DOI: 10.1016/S0927-796X(00)00024-3

DOI 10.12776/ams.v25i1.1215

- [14] D. Y. Ying, D. L. Zhang: Materials Science and Engineering A, Vol. 286, 2000, No. 1, p. 152-156, DOI: 10.1016/S0921-5093(00)00627-4
- [15] F. Shehata, A. Fathy, M. Abdelhameed, S. F. Moustafa: Materials and Design, Vol. 30, 2009, No. 7, p. 2756-2762, DOI: 10.1016/j.matdes.2008.10.005
- [16] F. Shehata, A. Fathy, M. Abdelhameed, S. F. Moustafa: Journal of Alloys and Compounds, Vol. 476, 2009, No. 1-2, p. 300-305, DOI: 10.1016/j.jallcom.2008.08.065
- [17] M. S. Motta, P. K. Jena, E. A. Brocchi, I. G. Solórzano: Materials Science and Engineering: C, Vol. 15, 2001, Issues 1-2, p. 175-177, DOI: 10.1016/S0928-4931(01)00272-7
- [18] P. K Jena, E.A Brocchi, M.S Motta: Materials Science and Engineering: A, Vol. 313, 2001, Issues 1–2, p. 180-186, DOI: 10.1016/S0921-5093(00)01998-5
- [19] M. R. Kracum et al.: Journal of the American Ceramic Society, 2018, p. 1-10, DOI: 10.1111/jace.15801
- [20] W. Hu, F. Donat, S. A. Scott, J. S. Dennis: RSC Advances, Vol. 6, 2016, No. 114, p. 113016-113024, DOI: 10.1039/C6RA22712K

#### Acknowledgements

*This research is funded by Hanoi University of Science and Technology (HUST) under project number T2017-PC-066.* 

# THE DEFORMATION OF AZ31 MAGNESIUM ALLOY DURING WARM CONSTRAINED GROOVE PRESSING

*Hue Thi Hong Dang*<sup>1</sup>*), Pham Thi Thuy*<sup>2</sup>*), Dao Minh Ngung*<sup>1</sup>*), Pham Quang*<sup>1</sup>*)\*, Valery Y. Shchukin*<sup>3</sup>*)* 

<sup>1)</sup> Hanoi University of Science and Technology, No.1 Daicoviet, Hanoi, Vietnam

<sup>2)</sup> Hanoi University of Mining and Geology, 18 Phovien, Bac Tu Liem, Hanoi, Vietnam

<sup>3)</sup> Belarusian National Technical University, Belarus

Received: 17.01.2019 Accepted: 26.02.2019

\**Corresponding author: e-mail: quang.pham@hust.edu.vn Tel.:* +84 888039303, *Hanoi University of Science and Technology, No.1 Daicoviet, Hanoi, Vietnam* 

# Abstract

A magnesium alloy AZ31 as plate of dimensions (60 x 60 x 3) mm has been constrained groove pressed (CGP) four deformation passes (16 pressings) at 250 °C by simulation and experiments. On the basis of the analysis of calculation results about the deformation distribution in the alloy AZ31 workpieces, the mechanism for its microstructure evolution during the severe plastic deformation (SPD) process was partly clarified. On the other hand, deformation heterogeneity distribution developed in the workpieces by applying CGP caused the evolution of a non-uniform microstructure. The TEM microstructure analysis results provided clear evidence that across the plate both the banded deformed microstructure where dislocation cell structure and/or partially or fully recovered polygonized subgrain microstructure are present. The recovering dynamic and local polygonization process contributes significantly to the formation of ultra-fine materials (UFG) microstructure.

Keywords: Finite Element Simulation, SPD, Constrained Grooved Pressing, AZ31 Magnesium Alloys, TEM

## 1 Introduction

Magnesium alloy is considered as an advanced material for many applications, especially in automotive, rail and aviation industries, with a low density advantage (1.74 g/cm<sup>3</sup>) and high thermal conductivity [1-3]. However, the morphology of the alloy is poor at room temperature because the crystalline lattice structure is tightly bound (h.c.p.), leading to limited deformability [4, 5]. However, the process of deformation by rolling, forging, pressing and polishing is still easy thanks to the mechanism of the mate and the operation of the slider at temperatures above 200 °C. During last decade, severe plastic deformation has been regarded as a viable method for producing nanostructured or ultra-fine materials [6-9]. Several methods have been proposed, developed and researched [10-12].

A severe plastic deformation method with great potential for the production of ultra-fine materials has been developed as a CGP [13, 14]. In 2001, Zhu undertook a SPD method based on the method of squeezing a flat metal plate with a cyclic groove die and then restoring the original planar shape to the flat die. Repetition of this process repeatedly causes large plastic deformation to accumulate in the sample without significantly altering the initial size (**Fig. 1**).



Fig. 1 Schematic representation of CGP process

The amount of plastic strain is dependent on the number of times and die geometry such as groove angle under the plane strain shear deformation using the equation (1.) of effective strain [18].

$$\varepsilon = n \frac{4}{\sqrt{3}} ln \left( \frac{r+t}{r+0.5t} \right) \text{ with } r = \frac{t}{\sin\theta}$$
(1.)

where, n is the number of time, t is the thickness of the workpiece and  $\theta$  is the groove angle. The variation of the groove angle of the die to changes in the deformation level of the workpiece. Effective strain ( $\varepsilon_{eff}$ ) is calculated by the equation [14].

$$\varepsilon_{eff} = \frac{\tan\theta}{\sqrt{3}} \tag{2.}$$

#### **2** Experimental materials and FEM methods

Although some experimental SPD and numerical simulation studies have been carried out on materials such as steel, copper, pure aluminum [15-18], but little is studying in the CGP publication.



Fig. 2 Die and workpiece used in FEM Fig. 3 Designed grooved die (a), flat die (b) simulation

ABAQUS software [19] was used in this study. On the basis of the size of the billet, the size of the mold, the mold and the detailed parts were calculated preliminary for the experiment. The

geometry of the 3D is driven directly on software Abaqus (**Fig. 2**). Abaqus offers several models for metal plasticity analysis. Main options include a choice between rate-independent and rate-dependent plasticity, a choice between the Mises yield surface for isotropic materials and Hill's yield surface for anisotropic materials. This decomposition can be used directly to formulate the plasticity model. Historically, an additive strain rate decomposition is:

$$\dot{\varepsilon} = \dot{\varepsilon}^{el} + \dot{\varepsilon}^{pl} \tag{3.}$$

Here  $\dot{\epsilon}$  is the total (mechanical) strain rate,  $\dot{\epsilon}^{el}$  is the elastic strain rate, and  $\dot{\epsilon}^{pl}$  is the plastic strain rate. This is intended for relatively high strain rate applications, such as dynamic events or metal forming process simulations. This type of rate dependence can be introduced in different ways. One way is to use an overstress power law [20]:

$$\frac{\dot{\varepsilon}^{pl}}{\varepsilon} = D \left(\frac{\overline{\sigma}}{\sigma^0} - 1\right)^n \quad for \quad \overline{\sigma} \ge \sigma^0 \tag{4.}$$

where  $\dot{\overline{\epsilon}}^{pl}$  is the equivalent plastic strain rate;  $\overline{\sigma}$  is the yield stress at nonzero plastic strain rate;  $\sigma^0(\varepsilon^{pl}, \theta, f_i)$  is the static yield stress (which may depend on the plastic strain  $(\varepsilon^{pl})$  via isotropic hardening, on the temperature  $(\theta)$  and on other field variables,  $(f_i)$ ; and  $D(\theta, f_i)$ ,  $n(\theta, f_i)$  are material parameters that can be functions of temperature and, possibly, of other predefined state variables.

The simulation the plate with geometry of  $(60 \times 60 \times 3)$  mm was modeled with total number of 3200 (CPE4RT) elements. The temperature of the workpiece and die are considered constant and equal to 250 °C. The pressing speed and coefficient of friction between the die and workpiece were taken to be 35 mm/s and 0.1 respectively. In the exprimental study magnesium alloy AZ31 commercial plates with dimensions of  $(60 \times 60 \times 3)$  mm were pressed up to 8 times using CGP approach. The chemical composition of the AZ31 is shown in **Table 1**. Before pressing, the specimen of AZ31 was annealed at 350 °C for 1 hr.

Element	Mg	Al	Si	Ca	Mn	Fe	Ni	Cu	Zn
Weight %	95.55	2.88	0.07	0.18	0.35	0.12	0.13	0.09	0.63

**Table 1** The chemical composition of the AZ31

**Fig. 3** is shown the designed grooved die with  $\theta = 45^{\circ}$  (top) and the designed flat (bottom). The material selected for die is SKD61 with heat treatment. The temperature selected on the die and sample during the CGP is 250 °C. The lubricant used in the experimental was MoS<sub>2</sub>. The whole pressing operation was carried out using a 100 ton hydraulic pressing machine. After straightening, the specimen is rotated 180° around the axis perpendicular to the plane of the sheet and then the first stage is repeated (**Fig. 1(III**)).

The specimen for transmission electron microscopy (TEM) were then selected from pressed plates, in order to evaluate the effect of straining on microstructure development. The selection of samples after the 8 deformation passes (16 pressings) were done from the top of the groove, which relates to an "undeformed" region (1), and from the inclined region, which relates to a sheared area, where equivalent strain of  $\varepsilon \sim 4.5$  was achieved (2 and 3), is shown in **Fig. 5 (a)**.

# 3 Results and Discusion

In the equation 1, with  $\theta = 45^{\circ}$  it was assumed that deformation occurring in the inclined regions is a simple shear and uniform. In this regard, the plastic strain introduced by shearing was

calculated simply by equation  $\gamma = tg(\theta)$ , where  $\theta$  is a inclination angle as shown in **Fig. 1**. This assumption leads to uniform plastic strain distribution after each 4n (n = 1, 2,...) deformation step. **Fig. 4** shows the simulated distribution of equivalent plastic strain in sample after pressing and flattening steps. Inspection of this figure reveals that after 4n pass, the imposed plastic strain on material is not uniform. Also the material between inclined parts of grooved die is deformed by shearing during pressing (the 1st step) and material between flat parts of die remains almost unreformed. As can be seen in this figure, the plastic strain distribution at inclined regions (the 1st step) is not uniform. This inhomogeneous distribution of strain at these regions finally (after every 4n steps) leads to an inhomogeneity in imposed plastic strain.

After first pressing (the 1st step) the imposed strain is inhomogeneous because only materials at inclined regions are subjected to severe deformation but regions between flat parts of die receive low plastic deformation. After 2nd step the inhomogeneity increases because the same regions are deformed during flattening. Before imposing 2nd step the plate is shifted one groove length to left or right and consequently during the 3rd and the 4th step the unreformed regions (during the 1st and the 2nd step) are subjected to severe deformation. This leads to improvement of plastic strain distribution in sample. Hence at every deformation cycle (each cycle comprises 4 steps), first pressing and flattening increase the inhomogeneity but second pressing and flattening improve the strain distribution.



Fig. 4 Equivalent plastic strain distribution in workpiece deformed up to 16 pressings

Analysing the microstructure by TEM in flat top (undeformed 1 area) the structure after first pressing consisted of elongated and/or equiaxed subbubgrains segmented by dislocatios. The presence of subgrains and dislocation cells substructure is evidence that in this region has this region has also undergone quite a large amount of plastic deformation and it can not be denoted as an "undeformed" area (**Fig. 5 (a**)). Observation over wide areas of the structure (flat area 1 and sheared 2 area) suggests that dislocation activities concerning the formation of low angle subgrain boundaries were already effective at he time of the first pressing. The detail of such transition where more distinctive low angle boundaries are apparent can be seen in **Fig. 5**. The development of a deformed substructure in the sheared area after completing the pressing and flattening process ( $\epsilon \sim 4.5$ ) is illustrated in **Fig. 5**. The microstructure consists of a banded arrangement of elongated subgrains, inside with dense dislocation network. Surprisingly, the small nuclei of polygonized subgrains were found along banded-like subgrains. A formation of polygonized dislocation-free



subgrains, after some cycles pressings and flattenings using tools (**Fig. 3**) is not common to find them in deformed structure.

Fig. 5 The mixture of subgrain structure within deformation bands

Completing the first deformation cycle, the cumulative strain becomes  $\varepsilon_{eff} \sim 1.12$  throughout the sample. The fragmentation of subgrains is apparent as well. The formation of new equi- axed "grains", deposisited along the subgrains was observed inside of deformed structure. The interior of these new grains is free of dislocations; grain boundaries are straight and they have a similar morphology to the already polygonized subgrains. The polygonization process is observed in AZ31 due to more intense plastic straining. The dislocation structure recovery and formation of polygonized grains was observed as a local process, which can be attributed also. When more intense straining was imposed the structural characteristics were similar, no matter whether four ( $\varepsilon_{eff} \sim 3.6$ ) or eight passes ( $\varepsilon_{eff} \sim 4.5$ ) were conducted. In the severely deformed areas the (banded) structure with mixture of deformation subgrains with high dislocation network and well developed polygonized subgrains were found (**Fig. 5**). The dislocation recovery effectively proceeds and dislocation annihilation is particularly evident. Locally observed, the more advanced process of polygonization contributed to formation of regular equiaxed subgrains free of dislocations. These

can then be the nuclei of new grains with high angle (**Fig. 5**). The arreas with polygonized were observed more frequently as strain increased. Considering transformation characteristics in the deformed structure, it appears that the mechanism, which becomes effective for microstructure refinement, involving grain subdivision and transformation of deformed subgrains to polygonized ones within shear bands, is local dynamic recovery and is not caused due to more advanced microshearing.

#### 4 Conclusions

Deformation inhomogeneity was studied in term of plastic strain distribution during deformation. It was found that after first pressing and flattening steps, the plastic strain is inhomogeneous but second pressing and flattening improve deformation distribution considerably.

On the other hand, deformation heterogeneity distribution developed in plate by applying CGP caused the evolution of a non-uniform microstructure. The TEM microstructure analysis results provided clear evidence that across the plate both the banded deformed microstructure where dislocation cell structure and/or partially or fully recovered polygonized subgrain microstructure are present. The dynamic recovery and local polygonization process contributes significantly to the formation of UFG microstructure. TEM microstructure analysis results indicate that there is a very low fraction of submicron grains with high angle grain boundaries even in case the strain applied is the highest.

## References

- Y. Kojima: Materials Transaction, Vol. 42, 2001, p. 1154–1159, DOI: 10.2320/matertrans.42.1154
- [2] A. Mwembela, E. B. Konopleva, H. J. McQueen: Scripta Materialia, Vol. 37, 1997, p. 1789 -1795, DOI: 10.1016/S1359-6462(97)00344-8
- [3] S. Schumann, H. Friedrich: Materials Science Forum, Vol. 419–420, 2003, p. 51–56, DOI: 10.4028/www.scientific.net/MSF.419-422.51
- [4] S. R. Agnew, O. Duygulu: International Journal of Plasticity, Vol. 21, 2005, p. 1161-1193, DOI: 10.1016/j.ijplas.2004.05.018
- [5] M. R. Barnett: Journal of Light Metals, Vol. 1, 2001, p. 167-177, DOI: 10.1016/S1471-5317(01)00010-4
- [6] R. Z. Valiev et. al.: Journal of The Minerals, Metals and Materials Society, Vol. 58, 2006, No. 4, p. 33-39, DOI: 10.1007/s11837-006-0213-7
- [7] Bidulská et al.: Chemicke Listy, Vol. 105, 2011, No. 16, p. 471-473
- [8] J. Bidulská, T. Kvačkaj, I. Pokorny, R. Bidulský, M. A. Grande: Archives of Metallurgy a Materials, Vol. 58, 2001, No. 2, p. 371-375, DOI: 10.2478/amm-2013-0002
- [9] Y. T. Zhu, T. G. Langdon: The Journal of The Minerals, Metals & Materials Society, Vol. 56, 2004, No. 10, p. 57-63, DOI: 10.1007/s11837-004-0294-0
- [10] R. Z. Valiev, R. K. Islamgaliev, I. V. Alexandrov: Progress in Materials Science, Vol. 45, No. 2, 2000, p. 103-189, DOI: 10.1016/S0079-6425(99)00007-9
- [11] T. Kvačkaj et al: Archives of Metallurgy a Materials, Vol. 58, 2013, No. 2, p. 407-412, DOI: 10.2478/amm-2013-0008
- [12] A. P. Zhilyaev, T. G. Langdon: Progress in Materials Science, Vol. 53, 2008, p. 893-979, DOI:10.1016/j.pmatsci.2008.03.002

- [13] Y. T. Zhu, T. C. Lowe, H. Jiang, J. Huang: Patent No. 6197129, USA, 2001
- [14] Y. T. Zhu, H. Jiang, J. Huang, T. C. Lowe: Metallurgical and Materials Transactions A, Vol. 32, 2001, p. 1559-1562, DOI: 10.1007/s11661-001-0245-0
- [15] T. C. Lowe, R. Z. Valiev: JOM, Vol. 56, 2004, No. 10, p. 64-77, DOI: 10.1007/s11837-004-0295
- [16] A. Azushima et al.: CIRP Annals-Manufacturing Technology, Vol. 57, 2008, No. 2, p. 716-735, DOI: 10.1016/j.cirp.2008.09.005
- [17] L. Olejnik, A. Rosochowski: Technical Science, Vol. 53, 2005, No. 4, p. 413-423
- [18] R. Z. Valiev, T. G. Langdon: Progress in Materials Science, Vol. 51, 2006, No. 7, p. 881-981, DOI: 10.1016/j.pmatsci.2006.02.003
- [19] Abaqus/CAE, Hibbit, Karlsson & Sorensen, Inc 2010, USA
- [20] Abaqus/Theory Manual, Hibbit, Karlsson & Sorensen, Inc 2010, USA

# Acknowledgements

Authors are grateful for the support by the B2016-BKA-26 project funded by the the Ministry of Education and Training of the Vietnam.

# STUDY OF BIOMASS UTILISATION IN THE IRON ORE SINTERING

Lina Kieush<sup>1)\*</sup>, Maksym Yaholnyk<sup>1)</sup>, Maksym Boyko<sup>1)</sup>, Andrii Koveria<sup>2)</sup>, Vladyslav Ihnatenko<sup>1)</sup> <sup>1)</sup> National Metallurgical Academy of Ukraine, Department of Iron Metallurgy, Dnipro, Ukraine <sup>2)</sup> National Technical University "Dnipro Polytechnic", Department of Chemistry, Dnipro, Ukraine

Received: 17.02.2019 Accepted: 08.03.2019

\*Corresponding author: e-mail: linakeush@gmail.com, Tel.: +380681768583, National Metallurgical Academy of Ukraine, Department of Iron Metallurgy, Dnipro, Ukraine

# Abstract

Dominating globally and within Ukraine, the blast-furnace practice for iron production requires iron ore sintering preparation wherein the significant amount of fossil fuel is consumed, accompanied by harmful emissions into the environment. Pursuing the purpose to mitigate this negative impact, we address the promising direction of biomass utilisation for a partial replacement of fossil fuels in iron ore sintering. This paper considers the benefits of fossil fuels substitution with biomass, the world practice of biomass utilisation in iron ore sintering and the scope of the biomass energy potential in Ukraine. The study for obtaining sinters with the use of raw biomass fuels (sunflower husk, walnut shell) and charcoal has been carried out via lab-scale sintering pot. The influence of various biomaterials types on the process of iron ore sintering have been investigated and the obtained sinter quality in comparison with the conventional types of the fuels allows establishing the feasibility of replacing 25 % of coke breeze by charcoal or by walnut shell. The sunflower husk application is possible if preliminary preparation of the material for increasing bulk density is assumed to be carried out, for instance, by pressing.

Keywords: iron ore sintering, biomass; sinter, walnut shell, sunflower husk, charcoal

#### 1 Introduction

Steel production in 2017 amounted approximately 1691.2 million tons, and according to the reported demand [1], in the nearest future this production will increasingly grow. Meanwhile, higher prices on conventional energy resources and their negative impact on the environment increase the share of renewable energy in the world. The use of biomass for energy based on contemporary technology is environmentally safer than the use of conventional energy from non-renewable sources such as coal. An important aspect is that the transition from fossil fuel sources to renewable sources will be more efficient through the use of local resources and already existing infrastructure [2-5].

One of the most promising types of renewable energy sources is biomass, which occupies the fourth place among fuels by value. Biomass is the only energy in the nature that contains a carbon resource in a fairly large quantity to be effectively used as a substitution of fossil fuels. Annually, biomass accounts for about 1.4 billion toe, which is about 14 % of the total primary energy consumption in the world. In the EU energy plans, the task is to increase the share of the energy produced from renewable energy sources in gross final energy consumption of up to 20 % by 2020, including those from biomass of up to 14 %. The same indicator in 2030 should be of 27 % [6].

According to the Bioenergy Association of Ukraine, the total potential of biomass energy was 20.2 million toe in 2015. The main constituents of this potential were the by-products of crop

production (straw of cereals and rapeseeds, corn stalks, sunflower, etc.) with the share of 37.6 % and energy crops (willow, poplar, miscanthus) of 39 % [7]. However, according to the State Statistics Service of Ukraine, the total supply of primary energy from biomass was only 2.2 % in the same 2015. Apparently, finding the ways to increase the share of biomass utilisation is becoming an urgent task since there is a significant reserve to increase the energy benefits from the biomass concentrated in the industries, the main consumers of energy resources. One of such industries is metallurgy.

The world's specialised scientific laboratories have been actively exploring the use of biomass instead of fossil fuels in various metallurgical processes over the last decade. The ways of utilisation for the biomass and the products of its processing in metallurgy are discussed in detail in works [8-11]. It is shown that, the use of biomass in metallurgical industries is complex in terms of scientific, technological and economic issues. Most important route for steel production is blast furnace/basic oxygen furnace (BF-BOF). The BF-BOF route represents about 70 % of the world steel production and, respectively, is the most fuel dependent. Therefore, the most effective approach in terms of  $CO_2$  mitigation and the replacement of conventional fuels and reducing agents can be considered the biomass utilisation in blast furnace ironmaking [12-16].

A number of works had been carried out over the efficiency issues of biomass application in the process of iron ore sintering. Ooi et al. [17] studied in detail the use of sunflower husks as an additional fuel incorporated in iron ore sintering. It was established that when replacing 10 % of coke breeze with the sunflower husk in sintering, there were no significant changes observed either in the combustion characteristics of the thereof process or in sinter quality. The use of charcoal instead of coke or coal during iron ore sintering increased the sintering velocity. This increase was explained to depend on the type of the biomass source and its share in the fuel component.

Generally, the efficiency of charcoal adding is known to be dependent on its origin and is reduced as follows: straw>wood>peat. Furthermore, the biomass addition reduces the maximum temperature of the layer of the materials being sintered and the time to achieve the maximum sintering temperature, and additionally it allows the expansion of sintering temperature range [18, 19]. It is important to note here that the changes in the combustion conditions and the gasification velocity produced by biomass application does not contribute to the formation of liquid calcium ferrite. This leads to the decrease in the sinter strength due to a smaller proportion of calcium ferrite in the mineralogical structure of the sinter [18, 20]. The same conclusion is made by Wei et al. [9], who indicates that, regardless the biomass type and its amount, the yield of the resulting sinter and its strength are reduced when the biomass participates in the sintering process. The possible mechanism for correcting the sintering process is the change in the size and the amount of the biomass, the amount of wind, as well as the properties of the biomass.

Generally, iron ore sintering is the source of a large number of harmful emissions, namely CO, CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub> and organic compounds [21-24]. Further, it has been established that the addition of sunflower husk reduces the formation of 2,3,7,8-polychlorinated dibenzo-para-dioxin and polychlorinated dibenzofuran by about 10 % (from 1 to 0.91 ng/nm<sup>3</sup>) [17]. In the case of replacing 20 % of coke with charcoal, the emissions of dioxins decrease by about 33 % [25, 26]. According to the study [18, 27], the use of charcoal obtained from straw and sawdust in quantities of 40, 20 and 15 wt.%, reduces SO<sub>2</sub> emissions by 38, 32 and 43 %, respectively, while NO<sub>x</sub> emissions are decreased by 27, 18 and 31 %, respectively. Consequently, the biomass utilisation can reduce the fossil fuels consumption and reduce harmful emissions. However, the negative effect of replacing coke with biomass is in the increase of CO content in the sinter gas [28, 29]. Thus, the CO concentration in gas increases from 2.07 % to 2.85–3.11% by volume for different types of biomass [27] and from 3.0 vol.% to 5.0 vol.% when using charcoal of different types, according

to [26]. Solving this issue is possible by changing the amount of air entering the combustion zone of fuel.

It is particularly noteworthy that the biomass application in metallurgy is known to reduce the formation of  $CO_2$  from fossil fuel. This effect is especially important in terms of the impact of metallurgical processes on climate change [30]. The primary attention is given to the report by Research Fund for Coal and Steel European Commission on the use of alternative carbon material in the sintering of iron ore [31]. The blast-furnace dust and slag, petroleum coke, anthracite, sunflower husks and olive stones are used as alternative fuels. According to the biomass research, the biomass fuel ground to the size smaller than the optimum size of coke breeze, contributes to the improvement of the temperature parameters of sintering, although the process performance and quality of the sinter are reported to be below that level when using coke breeze. Meanwhile, there is the main advantage of using biomass instead of a conventional fuel, it is the reduction of  $SO_2$  emissions and the improvement of the CO<sub>2</sub> balance.

The purpose of the present work is to study the influence of alternative fuels, namely plant biomass, on the iron ore sintering process and the quality of the sinter produced; to analyse the differences in the sintering process with biomass application in comparison with those incorporating the conventional fuels such as coke and anthracite.

# 2 Materials and Methods

For the course of the experimental studies, the following materials have been selected for the research: iron ore, iron ore concentrate, coke breeze, limestone, lime, anthracite, walnut shell, sunflower husk and wood charcoal. The chemical composition of the blend materials is given in **Table 1** while **Table 2** presents the proximate analysis of the fuels applied for the study.

	Content									
Materials	Fe <sub>total</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	LOI <sup>1</sup>	Other oxides	
Iron ore concentrate	65.88	28.27	62.71	6.44	0.30	0.17	0.26	1.85	-	
Iron ore	57.75	1.76	80.54	12.71	1.60	1.72	0.62	1.82	0.47	
Limestone	0.28	-	0.40	1.5	0.56	48.5	0.92	43.56	-	
Lime	12.66	-	18.09	1.8	26.61	86.8	1.40		-	

Table 1 Chemical Composition of the Blend Materials (wt.%)

<sup>1</sup>LOI – loss on ignition at 950 °C in air atmosphere.

Materials	Moisture, W <sup>a</sup>	Ash, A <sup>d</sup>	Volatile Matter, V <sup>d</sup>	Total Sulphur, St <sup>d</sup>	Fixed Carbon
Coke breeze	15.1	15.3	1.5	1.2	82.0
Anthracite	2.0	12.2	8.7	1.8	77.3
Charcoal	3.3	3.7	12.5	-	83.8
Walnut shell	7.2	0.3	75.6	0.2	23.9
Sunflower husk	8.0	2.6	73.0	-	24.4

**Table 2** Proximate Analysis of the Fuels (wt.%)

DOI 10.12776/ams.v25i1.1225

From **Table 2** it is obvious that the biomass analysed is characterised by a high content of volatile matter, but low ash content and almost no sulphur. It is worth noting that the largest fixed carbon content is a distinguishing feature of the charcoal.

The initial blend composition corresponded to the industrial blend. The content (in wt.%) of iron ore concentrate in the blend was 46.75, iron ore -10.5, limestone -10.25, lime -1.5 and coke breeze -6. The amount of the return applied in the blend for the sample preparation was 25 wt.%. In the case of using auxiliary fuel, the amount of fuel consumption has been calculated based on the fixed carbon and therefore different from the coke breeze.

The auxiliary fuels were used in individual form, as well as in mixtures with coke breeze in the following ratio (wt.%): 25/75, 50/50 and 75/25. **Table 3** shows the actual amount of the fuel in the blend (g), depending on the type of the material used when rounding the nearest whole number. For sintering process used 2 kg pelletized blend.

The ratio of the	Fuel type and quantity (g)							
fuel (wt.%)	Coke breeze	Anthracite	Charcoal	Walnut shell	Sunflower husk			
100	120	127	117	205	204			
75	90	96	88	154	153			
50	60	64	59	103	102			
25	30	32	29	51	51			

Table 3 The fuel amount in the sintering blend.

The materials were weighed, mixed, moistened, mixed again and pelletized in the pelletizer of the drum type. The water consumption for each sintering process with coke breeze was 7 wt.%, while in sintering experiments with other fuels the value of water varied, depending on the moisture content of the fuel. The pelletized blend was placed into the sintering pot equipped with a grate pre-wrapped in a bed of sinter with the fraction of 10-5 mm.

The sintering experiments were performed as described below. The initial underpressure was approximately 5 kPa. It should be noted that not in all cases the sintering process started exactly at the specified underpressure. This was due to the significant variations in the gas permeability of the blend column when using different types of fuel. Subsequently, in 60 s, the fuel ignition occurred to start the sintering process, and the ignition temperature was 1250 °C. During the sintering process, the temperature of the exhaust gases and pressure under the grate were controlled. Sintering was completed when the temperature of the exhaust gases reached the maximum and began to decrease. After the sintering process, the study of the obtained sinter was carried out. The abrasive strength and the impact strength indicators have been determined as the percentage of the content of the sinter fraction after the destructive load of less than 0.5 mm and more than 5 mm, respectively.

# 3 Results and Discussion

According to the results obtained with the sintering experiments, the main indicators of the sintering process, namely, the sinter quality and the specific capacity have been calculated. The changes in the pressures under the grate during the sintering process are shown in **Fig. 1**. In the Figures presented below anthracite, charcoal, walnut shell (WSH) or sunflower husk (SFH) are analysed individually in each case but referred generally as fuel.



Fig. 1 (a) Changing the underpressure in the case of using 100 % fuel; (b) Changing the underpressure in the case of using 50 % of coke breeze plus 50 % fuel; (c) Changing the underpressure in the case of using 75 % of coke breeze plus 25 % fuel; (d) Changing the underpressure in the case of using 25 % of coke breeze plus fuel 75 %.



Fig. 2 Dependence of the sinter yield on the fuel type



Fig. 3 Dependence of the sintering velocity on the type of fuel

As it can be seen, the addition of biomaterials to the sintering blend leads to an increase in the permeability of the sintered layer. This is due to the fact that the particles of biomaterials are located between the granules of the blend and increase the open porosity of the layer.

The dependences of the sinter yield and the sintering velocity on the biomaterial content are shown in **Fig. 2** and **Fig. 3**. Considering the influence of different types of solid fuels on the required sinter yield (+10 mm), its significant variations from 10 % to 75 % are noticeable. The lowest values have been obtained with the use of sunflower husks and walnut shell. The lowest values for sunflower husks can be explained by very low bulk density.

The results of measuring the bulk density of the biomaterials in comparison with anthracite and coke breeze are given in **Table 4**.

Type of fuel	Bulk density, kg/m <sup>3</sup>				
Sunflower husk	200				
Walnut shell	320				
Charcoal	285				
Coke breeze	340				
Anthracite	620				

Table 4 Bulk Density of Fuels

In addition to reducing the bulk density of the blend, with increasing amounts of biomaterials, the reactivity of the fuel increases. However, the sintering velocity also varies depending on the distribution of fuel in the blend and its size.

The indicators of sintering velocity increased dramatically when sunflower husks were used. The maximum temperature of the exhaust gases was 200-280 °C. This evidences the low temperature regime of the sintering process. Additionally, this is due to the shorter burning time of the biomaterials particles compared with coke and anthracite particles. Mnykh et al. [32] considered the change in the burning time of anthracite and coke particles in term of the dependence on their size and reported that for the standard size of fuel particles the combustion time of the coke breeze was 48-52 s and for the anthracite it was 72-76 s during sintering. However, in our experiments for the sunflower husks with the sizes up to 3 mm, the time of combustion did not exceed 40 s. As a result, it did not allow providing the required temperature for the sintering process. Consequently, in the case of lowering the temperature of the process, the amount of primary ore in the sinter increased, which led to the decrease in the content of hematite formed during the secondary oxidation of magnetite.

The low combustibility of anthracite enabled the incomplete consumption of fuel during the sintering process, namely, the amount of the residual carbon in the sinter made 10 % of its initial content in the blend.

**Fig. 4** shows the change in the specific capacity of the sintering pot, depending on the biomaterials content in the blend. It is known that the specific capacity of a sintering pot depends on the sinter yield and the sintering velocity. However, **Fig. 4** shows that despite the increase in the sintering velocity, the addition of biomaterials reduces the specific capacity of the sintering pot by reducing the sinter yield. Based on the results have been obtained and the above-mentioned information, we conclude that the substitution rate for charcoal or walnut shells is suitable as much as 25 %. In the case of using sunflower husks, the required specific capacity could not be reached in the sintering process. Therefore, this biomaterial requires preliminary preparation if there is the need for its further application in the iron ore sintering.



Fig. 4 Dependence of the specific capacity on the fuel type

**Fig. 5** shows the strength of the sinter for impact (a) and abrasion (b) but with sunflower husks. In this set of the experiments, we did not conduct any strength tests with the sinter obtained via the sunflower husks incorporations due to the very low sinter yield with this fuel though for the other experimental fuels the results are submitted below.



Fig. 5 (a) Dependence of the sinter impact strength on the fuel type; (b) Dependence of the sinter abrasion strength on the fuel type

The substitutive application of more than 50 % of charcoal or more than 25 % of walnut shell in the fuel causes the dramatic adverse effect produced on the resulting sinter impact strength due to the increasing porosity within the sinter. At the same time, these substitution rates allow sinter to possess the abrasion strength value and to exceed the values of coke breeze and anthracite. Eventually, based on the results of an experimental study of the alternative fuels influence on the basis of plant biomass in the iron ore sintering process and the quality of the obtained sinter, it has been established that charcoal or walnut shell can be used in the amount of 25 %. The sunflower husk utilisation is possible by pre-conditioning this material to increase its bulk density, for instance, by pressing.

## 4 Conclusions

The review in this work shows the possibilities of efficient biomass utilisation in the process of iron ore sintering. Such approach is able to improve the production and the environmental aspects

of the process. Due to the preparation and further application of the biomass with certain characteristics, it is possible to improve the thermal parameters of the sintering process, to increase the process productivity and to obtain sinter with the desired quality. The study on the influence of various biomaterials types on iron ore sintering process and the obtained sinter quality, in comparison with the conventional types of the fuels, allow establishing the feasibility of replacing 25 % of coke breeze by charcoal or the walnut shell. The use of the biofuels in such a ratio to the coke breeze enables sustaining the process efficiency and sinter strength at the required level.

The key characteristic of the biomaterials applied as a fuel for sintering is the bulk density, which determines the thermal parameters of the process, and the sinter structure. Therefore, in order to improve the technological indicators of the sintering process with biofuels utilisation, the preliminary preparation of biomaterials should be carried out with the purpose to increase their bulk density. Thus, the effective sunflower husk application is possible only with its preliminary preparation. Finally, the promising direction of improving the sintering technology with the biomaterials utilisation is the use of separate pelletizing methods.

### References

- World Steel Association. Short Range Outlook, 2018, [06.02.2019], Available online: https://www.worldsteel.org/media-centre/press-releases/2018/worldsteel-Short-Range-Outlook-2018-2019.html
- [2] Ukraine's promising market segments for heating with solid biomass (> 100 kW), [15.02.2019], Available online: http://www.bioenergy4business.eu/wpcontent/uploads/2015/06/B4B-WP2\_Country\_Summary\_Report\_Ukraine\_13-08-2015.pdf.
- [3] Biofuel use in Ironmaking from a Life Cycle Analysis Perspective, [15.02.2019], Available online: http://cancarb.ca/pdfs/CCRA\_papers/AISTech2011\_Biofuel%20LCA.pdf
- [4] P. Chudíková, M. Taušová, K. Erdélyiová, P. Tauš: Acta Montanistica Slovaca, Vol. 15, No. 2, 2011, p. 139-145, (in Slovak)
- [5] P. Tauš, M. Taušová, P. Horbaj, K. Čulková, J. Koščo: Economic evaluation of boiler for biomass using in Slovakia, In.: International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM, Vol. 1, 2015, No. 4, p. 167-174
- [6] Bioenergy instead of gas., [06.02.2019], Available online: http://www.epravda.com.ua/publications/2015/01/9/520368/, (in Ukrainian)
- [7] H. Heletukha, S. Drahniev, P. Kucheruk, Y. Matvieiev: Practical manual on the biomass utilisation as a fuel in the municipal sector of Ukraine (for representatives of the agroindustrial complex), Agency for Renewable Energy, Kyiv, Ukraine, 2017, (in Ukrainian).
- [8] E. Mousa, C. Wang, J. Riesbeck, M. Larsson: Renewable and Sustainable Energy Reviews, Vol. 65, 2016, p. 1247-1266, DOI: 10.1016/j.rser.2016.07.061
- [9] R. Wei, L. Zhang, D. Cang, J. Li, X. Li, C.C. Xu: Renewable and Sustainable Energy Reviews, Vol. 68, 2017, No. 1, p. 511-524, DOI: 10.1016/j.rser.2016.10.013
- [10] H. Suopajärvi, A. Kemppainen, J. Haapakangas, T. Fabritius: Journal of Cleaner Production, Vol. 148, 2017, p. 709-734, DOI: 10.1016/j.jclepro.2017.02.029
- [11]C.M. Wiklund: Optimization of a steel plant utilizing converted biomass. PhD Thesis. Turku/Abo: Åbo Akademi University, Finland, 2016
- [12] W. Wei, P. Mellin, W. Yang, C. Wang, A. Hultgren, H. Salman: Utilization of biomass for blast furnace in Sweden: biomass availability and upgrading technologies. Stockholm, 2013, Report I:1, DOI: 10.1016/j.egypro.2014.12.125

DOI 10.12776/ams.v25i1.1225

- [13] E. A. Mousa, H. M. Ahmed, N. N. Viswanathan, M. Larsson: Recent trends in ironmaking blast furnace technology to mitigate CO<sub>2</sub> emissions: tuyeres injection. In.: Ironmaking and steelmaking processes, edited by P. Cavaliere, Springer, Switzerland, 2016, p. 173-197, DOI: 10.1007/978-3-319-39529-6
- [14] H. Suopajarvi: Bioreducer use in blast furnace ironmaking in Finland. PhD Thesis, Oulu University, Oulu, 2014
- [15] H. Helle, M. Helle, H. Saxén, F. Pettersson: ISIJ International, Vol. 49, 2009, No. 9, p. 1316-1324, DOI: 10.2355/isijinternational.49.1316
- [16] K.W. Ng, W.P. Hutny, J.A. MacPhee, J.F. Grandsen, J.T. Price: Bio-fuels use in blast furnace ironmaking to mitigate GHG emission. In.: 16th European Biomass Conference and Exhibition, Valencia, Spain, June 2-6, 2008
- [17] T. Ch. Ooi et al.: Miner Eng, Vol. 21, 2008, p. 167-177, DOI: 10.1016/j.mineng.2007.09.005
- [18] M. Gan: Fundamental research on iron ore sintering with biomass energy. PhD Thesis. Changsha: Central South University, Hunan, 2012
- [19] M. Zandi, M. Martinez-Pacheco, T.A.T. Fray: Minerals Engineering, Vol. 23, 2010, No. 14, p. 1139-1145, DOI: 10.1016/j.mineng.2010.07.010
- [20] R. Lovel, K. Vining, M. Dell'Amico: Mineral Processing and Extractive Metallurgy Review, Vol. 116, 2007, No. 2, p. 85-92, DOI: 10.1179/174328507X163887
- [21]G. Liu et al.: Chemosphere, Vol. 89, 2012, No. 4, p. 467-472, DOI: 10.1016/j.chemosphere.2012.05.101
- [22] C. Mo, C. Teo, I. Hamilton, J. Morrison: ISIJ International, Vol. 37, 1997, No. 4, p. 350-357, DOI: 10.2355/isijinternational.37.350
- [23] Y.S. Mok, I. Nam: IEEE Transactions on Plasma Science, Vol. 27, 1999, No. 4, p. 1188-1196, DOI: 10.1109/27.782299
- [24] Y. Chen et al.: Chemosphere, Vol. 88, 2012, No. 11, p. 1324-1331, DOI: 10.1016/j.chemosphere.2012.05.031
- [25] T. C. Ooi, D. Thompson, D. R. Anderson, R. Fisher, T. Fray, M. Zandi: Combustion and Flame, Vol. 158, 2011, No. 5, p. 979-987, DOI: 10.1016/j.combustflame.2011.01.020
- [26] T. Kawaguchi, M. Hara: ISIJ International, Vol. 53, 2013, No. 9, p. 1599-1606, DOI: 10.2355/isijinternational.53.1599
- [27] M. Gan et al.: ISIJ International, Vol. 52, 2012, No. 9, p. 1574-1578, DOI: 10.2355/isijinternational.52.1574
- [28] J. G. M. S. Machado, E. Osório, A. C. F. Vilela, A. Babich, D. Senk, H. W. Gudenau: Steel Research International, Vol. 81, 2010, No. 1, p. 9-17, DOI: 10.1002/srin.200900093
- [29] L. Lu et al.: ISIJ International, Vol. 53, 2013, No. 9, p. 1607-1616, DOI: 10.2355/isijinternational.53.1607
- [30] T. Norgate, N. Haque, M. Somerville, S. Jahanshahi: ISIJ International, Vol. 52, 2012, No. 8, p. 1472-1481, DOI: 10.2355/isijinternational.52.1472
- [31]European Commission. EUR 25151. Alternate carbon sources for sintering of iron ore (Acasos), Research Fund for Coal and Steel, Luxembourg, Publications Office of the European Union, 2013, DOI:10.2777/58105
- [32] A. S. Mnykh, I. G. Yakovleva, M. Yu. Pazyuk: Energy Saving Power Engineering Energy audit, Vol. 10, 2015, p. 56-63, (in Russian)

## Acknowledgements

This research was funded by the Ministry of Education and Science of Ukraine, grant number 0117U003919. Additionally, the authors would like to acknowledge Prof. Arkadii Tarakanov, Head of Department of Iron Metallurgy, National Metallurgical Academy of Ukraine for his kind support in carrying out this work.

# THEORETICAL-EXPERIMENTAL POSSIBILLITIES OF MICROSTRUCTURE QUANTIFICATION OF DISPERSION STRENGTHENED MATERIALS

Michal Besterci<sup>1)\*</sup>, Katarína Sülleiová<sup>1)</sup>

<sup>1)</sup> Institute of Materials Research of Slovak Academy of Sciences, Košice, Slovak Republic

Received: 14.12.2018 Accepted: 28.02.2019

\*Corresponding author: e-mail: mbesterci@saske.sk Tel.: +421 55 692241, Institute of Materials Research of Slovak Academy of Sciences, Košice, Watsonova 47, 040 01 Košice, Slovak Republic

# Abstract

The present paper is devoted to the possibilities to classify the spatial arrangement of the elements (features) of a stochastic process with geometrical objects. The fundamental quantities describing point processes were introduced. Experimental possibilities of structural objects determination, possibilities of evaluation of the size distribution of the secondary phases, testing of planar point structures (estimation of the process intensity, square method and characteristics of the second order) were estimated. Interparticle distances, namely mean interparticle distance, mean minimum distance, mean visibility and mean path of spherical contact were defined. Selected processes were described and demonstrated from simulated realizations on  $Al-Al_4C_3$  dispersion strengthened material, prepared by a powder metallurgy method of reaction milling. Interparticle distances of  $Al_4C_3$  particles were evaluated. Polygonal methods and quadrant counts method were used for characterization of the particle arrangement.

Keywords: mechanical alloying, structure parameters, interparticle distance, testing of planar point structure

#### 1 Introduction

Intensive research and development of new materials and their challenging technologies belong among those matters which become determining for the recent worldwide industrial and economical progress. They lead to a considerable diversification of materials which makes the choice of the optimal material for any considered application possible.

The research proceeds in several directions the most important of which are new metallic alloys, ceramics, polymers, composites and amorphous materials. The composite materials with metallic, plastic and ceramic bases have already found their application in the machine industry, but their wider use is still limited by insufficient automation on their production resulting in their cost and by the need to elaborate new designs and techniques adapted for a better understanding and influencing of their properties, [1-8].

The mechanism of dispersion strengthening is based on the presence of a low volume fraction of fine secondary particles in the metal matrix, [9 - 11]. If the particle sizes are negligible, with respect to their mutual distances, they can be considered as points. Particles in real material can be visualized in the cross section of the microstructure by optical microscopy and scanning electron microscopy (SEM) or in a projection by transmission electron microscopy (TEM). Quantitative characterization of the particle space distribution is a significant problem, [12-14]. Classification of the Al<sub>4</sub>C<sub>3</sub> particle arrangement in Al-Al<sub>4</sub>C<sub>3</sub> materials with 2 wt. % Al<sub>4</sub>C<sub>3</sub> using the stochastic geometry method was the aim of the paper.

#### 2 Experimental possibilities of determination of structural objects

Experimental determination of the basic structural parameters of the materials strengthened by particles is very important and demanding from the experimental point of view. Therefore, some situations and principal possibilities of obtaining the information mainly on the volume fraction of dispersion particles and on their size distribution were analyzed. Let us assume further the spherical particles distributed in space in the uniform stochastic manner. Let us to define the total volume fraction  $f_v$ . The particle size is defined by the probability density function h(d).

# a) Plane metallographic section through the structure

The plane section through the structure in question represents the two-dimensional space with circular particles; their volume fraction is  $f_A$  and the probability density function of the particle sizes in the plane is g(d). In this case, the well-known stereological relationship  $f_v = f_A$  is valid. Moreover, it is possible to prove that  $\lambda_3 = \lambda_2$  [15], which allows theoretically the direct experimental determination of the mean interparticle distance  $\lambda$ . The distance  $(A_{min})$  cannot be

determined from the plane section for general distribution of the particles in space. For monodispersion systems, it is possible to find the relation between the planar and volume density of particles, and to determine the distance  $\Lambda_3$  on the basis of the known value of the planar density. However, for polydispersion systems, it is necessary to know the shape of the function h(d) on the basis of plane sections, in order to determine the mean particle distance  $\Lambda_3$ . This task can be solved, and is discussed in the paper [16]. On the basis of the plane sections, it is also possible to determine other individual and global characteristics of particles.

The sizes of particles of the dispersion strengthened systems, which were prepared by internal oxidation, or by chemical precipitation, ranged below 100 nm. The sizes of the effective particles (~70%) of the systems, which were prepared by reaction milling, were below 200 nm. The above described methods, which give sufficient information, cannot be used for the resolution of an optical microscope, nor can be used for the whole range of granulometric composition of the particles, They can be used only for estimation of the largest particles, which do not have the decisive influence on mechanical properties.

#### b) Extraction carbon replicas

Contrary to the plane metallographical section, a structure, in which the "two-dimensional particles" do not represent the plane sections through the three-dimensional particles, but only the projections of particles to a plane, was studied. The original Asby-Eberling model [17] assumes that all particles, which have the intersection with the plane (the depth of matrix etching below this plane is larger than the maximum size of the particles), are included in the replica. In this case, the probability density function of projections of particles g(d) can be determined experimentally. The following relationship is valid between the functions g(d) and h(d):

$$g(d) = \frac{dh(d)}{\int_0^\infty dh(d)dd}$$
(1.)

which allows the shape of the function h(d) to be determined.

It is then possible, on the basis of the planar density of particles and using function h(d), to determine the volume density of particles and the distances  $\lambda_3$ , or  $\Lambda_3$ , respectively. If the etching depth is smaller than  $d_{max}$ , some of the particles will not be "trapped" in the replica, but a print will be formed. This case has been analyzed by Horalek [18]. Further information is then necessary to determine the form of the function h(d) (the depth of etching, general form of the function h(d), the number of particles, which are not included in the replica, but only printed).

Moreover, the basic model is idealized. In the real material, the situation is complicated, both by non-uniform etching and by the presence of the accumulated particles. If the clusters of accumulated particles are present on the replicas, then we can use them for rough estimation of the form of the function h(d) in such a way that they are considered to be the random sampling from the set of particles. In addition, the accumulated particles can serve as the low limit of estimation of the etching depth.

# c) Thin foil

This case is the simplest one from the theoretical point of view. Projections of the particles in a plane by examination of the foil by the electron beam were obtained. The function h(d) can be determined directly on the basis of the assumptions of the particle shape. However, in real experiments, the problem of measuring the thickness of the foil at the examined point arises. In addition, there is a problem of behavior of the particles in the surface layers of the foil under reduction of its thickness, as well as the problem of overlapping particles. These problems can be partially solved using a goniometer and a scanning adapter on a transmission electron microscope. In spite of the above facts, it is necessary to regard the thin foil as the most reliable source of information, mainly on the finest fractions of the dispersion phase.

### 3 Models of heterogeneous structures and their evaluation

The conventional parameters, such as volume fraction and interparticle distance, do not depend on the spatial arrangement of the particles and should be replaced by other variables, which are sensitive to the structure. These include various types of stochastic free paths, at which more direct physical interpretation is assumed in connection with the transport processes. From this point of view, various models of the spatial arrangement of particles (stochastic closed sets, combined sets of particles with the given probable distribution of the shape, size and positions) are analyzed in the monograph [19]. The results include stochastic systems, which do not influence each other, stochastic clusters, homogeneous systems of particles, homogeneous systems with defects (vacancies, interstices, pores, foreign particles) and they are documented by numerous diagrams. General solution of this problem allows the results to be applied to the linear, planar and spatial systems, respectively.

# 3.1 Possibilities of evaluation of the secondary phases distribution

The mechanism of dispersion strengthening is based on the presence of a relatively small quantity of fine particles in the matrix. If the size of these particles is substantially smaller than their distances, they can be considered, in the first approach, as the "point" objects from the viewpoint of their distribution. Their distribution in the matrix can play an important role at their effects on the process taking place in the matrix.

It is necessary to realize that the particles of certain sizes and shapes are arranged in space in the real dispersion strengthened material. In order to make them visible, a section through the microstructure can be made (metallography or SEM), or to depict them in their projection using transmission electron microscopy (TEM). The signs of the spatial distribution of the real particles of sizes different from zero are manifested in both the section and in the projection, but the signs of the distribution of the point particles are manifested only in the projection. The quantitative characterization of the spatial distribution of particles is very important task. It was used only sporadically in physical metallurgy. The basic stochastic models of the spatial distribution of particles are as follows:

a) The Poisson point process, which serves as a reference of stochastic distribution of points, is defined as the position of an arbitrary point, which does not depend on the position of other points.

- b) The hard-core model, for which the condition requiring that the distance of two arbitrary points of the process is larger than the value determined in advance.
- c) The cluster model, which can be created on the basis of the Poisson point process in such a way that each point of the system is replaced by a cluster of points.
- d) The grid arrangement of points with defects, such as interstices, vacancies and displacement of points from their equilibrium position.

The following two methods are often used for evaluation of the spatial distribution of particles. With the first method, the point planar processes are tested, the second one is based on the term of the interparticle distance.

# **3.2 Testing of planar point structures**

#### a) Estimation of process intensity

The question is about the estimation of the number of points in the unit of the area studied assuming the homogeneous structure. Accuracy of the standard used procedure (the ratio between the number of points and the surface measured) depends strongly on the type of points distribution. For the usually used level of estimation (95%) about 1600 points are needed in the area to obtain the ideal stochastic distribution (Poisson point process). If a large number of clusters of points are present, the number of objects must be considerably greater in order to obtain the above accuracy [20].

#### b) Square method

The area studied is divided into a large number of subareas of the same size, in which the number of points is ascertained. On the basis of the mean number of points and their dispersion in these subareas, various statistics are prepared (index of dispersion, cluster size index, Greig-Smith test and others), which can indicate a tendency of points towards clustering, or towards regular arrangement respectively. It is necessary to realize for all indices that their value depends not only on the distribution of points, but on the size of subareas as well. Therefore, it is recommended to evaluate also the dependence of the index on the size of the subareas.

#### c) Characteristics of the second order

These characteristics describe in detail the spatial distribution of points. They can be determined using, for example, the K-function K(r), whose course is given by the dependence between the number of points in the circular surrounding *r* of the typical process point on the size of *r*. The *L*-function is also used, which is defined by the relationship  $L(r) = (K(r)/\pi)^{1/2}$ , and the pair correlation function g(r), which characterizes the change rate K(r) in dependence on *r*,  $g(r) = (2\pi r)^{-1/2} dk/dr$ ; for the planar Poisson point process, the following is valid:  $K(r) = \pi^2$ , g(r) = 1 and L(r) = r.

Information on the spatial distribution of particles in relation to their sizes and on the spatial distribution of the volume fraction are then obtained.

#### **3.3 Interparticle distances**

Problems of the definition of the interparticle distances both for the monodispersion and polydispersion set of the spherical particles were discussed in the previous section. One of the conclusions of the papers says that the only parameter (mean value) used to characterize the granulometric composition of the dispersoid in the real polydispersion systems can distort the theoretical estimation of the interparticle distance of the type  $\lambda_{\mu}$ . When one uses the term "interparticle distance", it is necessary to realize, (e.g. for characterization of materials or processes which take place in them) that this term is rather intuitive, and has no generally valid,

universal definition. Therefore, it cannot be assigned the generally valid range of values. At first, we must select one of the exactly defined types of "distances" considering the process studied and to interpret or compare their properties within the selected framework.

# a) Mean interparticle distance $\lambda_{\mu}$

This is the mean value of chord lengths of the generated systems of isotropic uniform stochastic straight lines intersecting the object studied. It is often referred to as the "mean free path" between the particles. Its "positive" property is that after observing the condition of stochasticity of the system of plane sections through the volume structure, it is possible to prove that  $(\lambda_{\mu})_3 = (\lambda_{\mu})_2$  (i.e.  $\lambda_{\mu}$  of the sample equals  $\lambda_{\mu}$  of its isotropic, uniformly stochastic plane sections), which has contributed to its frequent use. However, its negative property is that it does not depend on the spatial distribution of the particles, because it is a global variable, which is fully determined by the total volume and surface of the sample particles.

# b) Mean minimum distance $\lambda_p$

This is the mean value of the distance between the nearest particles. Its advantage is based on the fact that it is well worked out for the Poisson stochastic process, however, the mechanical use of these theoretically derived relations for any other structure is confusing. It is necessary to state that this parameter describes well the distance within the particle clusters, however, it has no informative ability, therefore its physical and metallurgical interpretation is problematic.

# c) Mean visibility $\lambda_{\nu}$

This is the mean value of the distance from the randomly selected point of the matrix to the nearest particle in the randomly selected direction. This distance can be described as the "mean visibility in a forest" (for the plane case). Its properties, mainly the relation between the distance in the volume and the respective plane section, have not been theoretically worked out yet. Physical and metallurgical interpretations in relation to the obstacles for dislocation movements are also problematic.

# d) Mean path of spherical contact $\lambda_v$

This is the mean value of the distance from the randomly selected point of the matrix to the nearest particle. It determines the distribution of sizes of the maximum spheres inscribed into the matrix in its internal points; therefore, it depends on the spatial distribution of particles [20]. It has suitable limit properties, and can be easily measured manually. From the physical and metallurgical viewpoint, it can be interpreted, for example, as the characteristic of the minimum diameters of dislocation loops of the emitted F-R sources. Therefore, we consider it to be the optimum distance of particles in the dispersion strengthened systems.

However, it is necessary to state that at the quantification of the heterogeneous systems with particles, the mean distance, which was determined as the cube root of the average volume per one particle, was frequently used. It is determined by the number of particles in the volume unit and does not depend on the spatial distribution of particles. The differences in the values of the interparticle distances defined in such a way are documented in **Fig. 1**, where their mean values are plotted in the simulated Boolean model of spherical particles (the Boolean model is created by substitutions of models of particles with various shapes for individual points of any point process). In our previous works [19, 21, 22] the distances between the particles by point object simulation methods were evaluated. This included the mean interparticle distance  $\lambda_{\mu}$ , the mean minimum distance  $\lambda_{\rho}$ , the mean visibility  $\lambda_{\nu}$ , and the mean free spherical contact distance  $\lambda_{g}$ . The characteristics and properties of these parameters have been analyzed in [21]. The mean free spherical contact distance  $\lambda_{g}$  was the optimal parameter which had a physical interpretation, too.

During the last years, a new approach to the description of point systems has been developed intensively, which was referred to as polygonal methods [22]. The composite system Al-Al<sub>4</sub>C<sub>3</sub> prepared by powder metallurgy was used for the experiments. The starting powders Al (of size < 100  $\mu$ m) and C (2 wt. %) were dry mechanically alloyed for 90 minutes, compacted under the pressure of 600 MPa (rod diameter 40 mm), annealed at 550°C/3hr and then extruded with 94% diameter reduction; the resulting volume fraction of Al-Al<sub>4</sub>C<sub>3</sub> was  $V_V = 8\%$ , roughly one third of  $V_V$  was comprised in very coarse particles. Thin foils if the thickness L= (2000 ± 500) Å were prepared by spark cutting followed by electropolishing and did not include coarse particles.



Fig. 1 Schematic illustration of interparticle distances

Properties of Voronoi tessellation and their various generalizations were studied in the monograph [23]. The dual representation formed in the above way described completely the given point system. Intermediate stages of evaluation for thin foil (a), outlines of particles (b), and of reference points (c) were documented in **Fig. 2**.



Fig. 2 Intermediate stages of evaluation for thin foil (a), outlines of particles (b) and reference points (c)

The practice of the polygonal methods in describing the spatial arrangement of particles is explained in detail, namely momentum analysis, order statistics and parametric estimation of the

probabilistic distribution, all in the relation to the cell areas of the Voronoi tessellation generated by the reference points of the particles. The polygonal approach is then applied to four samples, **Fig. 3** – TEM projections of thin foils of an aluminium based dispersed alloy with quasiglobular particles. The main advantages of the method are stressed: reliable characteristics of the arrangement can be obtained on the basis of relatively small samples and without the accurate knowledge of the thin foil thickness. Moreover, the sensitivity is higher in comparison with more standard approaches (e.g. quadrant counts), [24 - 28].



**Fig. 3** Voronoi mosaics generated by point patterns (a), (b), (c) and (d)

# 4 Conclusions

General problems of testing the structure of materials produced by PM technology were summarized as well as possibilities of the quantitative estimation of structure parameters and basic problems connected with the experimental techniques:

- 1. Models of heterogeneous structures and approaches of quantitative evaluation of secondary phases by stereological methods (squares method, dual method by means of Voronoi mosaics) were defined.
- 2. Analysis of particle interface in thin foils of Al-Al<sub>4</sub>C<sub>3</sub> materials was realized. TEM images of thin foils with quasi-globular particles were examined by means of two methods of spatial statistics. The spatial arrangement of particle reference points was described by means of quadrate count statistics and by polygonal method (the analysis of the Voronoi mosaic generated by patterns of particle reference points). A good agreement between the both approaches was found, the polygonal method was more sensitive and its results were more conclusive.
- 3. Six important types of interparticle distances based mainly on the concept of matrix free paths or rays were introduced. The distribution functions and probability density functions of the path and ray lengths as well as the expressions for the first two moments of these distributions were deduced for the Poisson point process and Boolean model.

#### References

- T. Kvačkaj et al.: Materials Characterization, Vol.134, 2017, p. 246-252, DOI: 10.1016/j.matchar.2017.10.030
- [2] T. Kvačkaj et al.: Archives of Metallurgy and Materials, Vol. 58, 2013, No. 2, p. 407-412, DOI: 10.2478/amm-2013-0008
- [3] D. Manfredi, R. Bidulský: Acta Metallurgica Slovaca, Vol. 23, 2017, No. 3, p. 276-282, DOI: 10.12776/ams.v23i3.988
- P. Petroušek et al.: Acta Metallurgica Slovaca, Vol. 21, 2015, No. 3, p. 176-183, DOI: 10.12776/ams.v21i3.615

DOI 10.12776/ams.v25i1.1233

- [5] T. Kvačkaj, R. Kočiško, J. Bidulská, M. Luptak, A. Kováčová: Acta Physica Polonica A, Vol. 131, 2017, No. 5, p. 1315-1318, DOI: 10.12693/APhysPolA.131.1315
- [6] R. Bidulský, M. Actis, M. Kabátová, J. Bidulská: Journal of Materials Science & Technology, Vol. 25, 2009, No. 5, p. 607-610
- [7] A. Fedorikova et al.: Acta Metallurgica Slovaca, Vol. 22, 2016, No. 2, p. 102-110, DOI: 10.12776/ams.v22i2.616
- [8] R. Bidulský, M. Actis, L. Ferraris, P. Ferraris, J. Bidulská: Acta Physica Polonica A, Vol. 118, 2010, No. 5, p. 802-803, DOI: 10.12693/APhysPolA.118.802
- [9] I. Saxl: Stereology of Objects with Internal Structure, Elsevier, ISBN 0444416854, 1989
- [10] M. Besterci: Dispersion Strengthened Al Prepared by Mechanical Alloying, Cambridge Int. Sci. Publ., 1999, ISBN 189832655
- [11] T. Weiβgäerber, B. Kieback: Materials Science Forum, Vol. 343, 2000, p. 275-283, DOI: 10.4028/www.scientific.net/MSF.343-346.275
- [12] J. Bidulská, T. Kvačkaj, I. Pokorny, R. Bidulský, M. Actis Grande: Archives of Metallurgy and Materials, Vol. 58, 2013, No. 2, p. 371-375, DOI: 10.2478/amm-2013-0002
- [13] J. Bidulská, T. Kvačkaj, R. Bidulský, M. Actis Grande, L. Litynska-Dobrzynska, J. Dutkiewicz: Chemicke Listy, Vol. 105, 2011, p. s471-s473
- [14] J. Bidulská, T. Kvačkaj, R. Bidulský, M. Actis Grande: Acta Physica Polonica A, Vol. 122, 2012, No. 3, p. 553-556, DOI: 10.12693/APhysPolA.122.553
- [15] M. Besterci, K. Pelikán: Kovové materiály, Vol. 4, 1985, p. 497-501
- [16] E. E. Underwood: *Quantitative Stereology*, Addison-Wesley Publ. Co., Reading, Massachusetts, 1970
- [17] M.F. Ashby, R. Eberling: Transactions of the Metallurgical Society of AIME, Vol. 236, 1966, p. 1396-1401
- [18] J. Horalek: Kovové Materiály, 3, 1982, p. 195
- [19] I. Saxl, K. Pelikán, J. Rataj, M. Besterci: *Quantification and Modelling of Heterogeneous Systems*. Cambridge Interscience Publ., ISBN 1898326045, 1995
- [20] I. Saxl, K. Pelikán, M. Besterci, J. Rataj: Testing and Modelling Structures of Heterogeneous Systems, Pokroky práškové metalurgie, Vol. 1-2, Šumperk, 1990
- [21] I. Saxl, M. Besterci, K. Pelikán: Pokroky práškové metalurgie, Vol. 3, 1986
- [22] M. Besterci, I. Kohútek, I. Saxl, K. Sülleiová: Journal of Materials Science, Vol. 34, 1999, p. 1055-1060, DOI: 10.1023/A:1004552213455
- [23] A. Okabe, B. Boots, K. Sugihara: Spatial Tessellations: Concepts and Applications of Voronoi Diagrams, J. Wiley, Chichester (1992), ISBN: 0-471-9340-5
- [24] M. Besterci, I. Kohútek, I. Saxl, K. Sülleiová: Kovové materiály, Vol. 33, 1995, No. 4, p. 251-268
- [25] M. Besterci, J. Zrník, M. Šlesár: Kovové materiály, Vol. 35, 1997, p. 344-349
- [26] M. Besterci, O. Velgosová, J. Ivan, L. Kováč: Kovové materiály, Vol. 39, 2001, p. 309-315
- [27] M. Besterci, O. Velgosová, I. Kohútek: Iranian Journal of Science & Technology, Transaction B, Vol. 28, 2002, No.B2, p. 233-238
- [28] M. Besterci et al.: Nanostructural Al Composites, Lambert Academic Publishing, 2015, ISBN-10: 3659773875

#### Acknowledgements

The work was supported by the Slovak National Grant Agency under the Project VEGA 2/0080/17.

DOI 10.12776/ams.v25i1.1233

# ANALYSIS OF THE QUALITY OF MOISTENING OF THE SINTER MIX IN THE DRUM PELLETIZER

Sergey Krivenko<sup>1)\*</sup> <sup>1)</sup> Mariupol State University, Faculty of Law and Economics, Mariupol, Ukraine

Received: 15.10.2018 Accepted: 21.01.2019

\* Corresponding author:e-mail: booktwix@gmail.com Tel.: +380 96 757 4547, Department of Mathematical Methods and System Analysis, Faculty of Law and Economics, 129a, Budivelnykiv Ave., Mariupol, Ukraine, 87500

# Abstract

The analysis of changes in moisture, equivalent diameter of the granules, layer porosity and size variation under the abrupt perturbing effect on the input humidity of the charge was made. The change in other parameters from the charge moisture lags about 30 seconds. This is due to different mass transfer rates for moisture and fine fractions. PI-controller settings for control of all measured parameters were calculated. The best indicators of the transition process comply with the control of moisture content of the charge. However, the most representative is the simultaneous control of these parameters. A new indicator of the effectiveness of the shower unit of the pelletizer drum is developed, based on the difference in the rates of mass transfer of moisture and solid particles. The value of this indicator should be kept to a minimum.

Keywords: pelletizer, moisture, equivalent diameter, porosity, variation

#### 1 Introduction

The most efficient modes of sintering, which correspond to Voice principle (equality of speeds of movement of the fronts of heat transfer and combustion of fuel mixture) to the success of the process of agglomeration of iron ore materials is necessary to ensure [1, 2]. Production of high-quality sinter and high performance is impossible without proper control of the gas-dynamic properties of the sintered layer. Pelletizing, which forms the final fractional composition of the charge before loading onto the pallets of the sintering machine, is one of the main technological stages of preparation of the charge for sintering. The quality of pelletizing depends on many factors: the fractional composition of the initial charge and its hydrophilic properties, the amount of moisture in the pelletizer, the properties of the shower device and the pelletizer drum, etc. Extensive method by increasing the drum length up to 12 m. to improve the fractional characteristics of the charge is used most often. Of course this has a positive effect, but does not exclude the use of intensive methods. Therefore, works aimed at improving the quality of pelletizing are relevant and require further development.

The purpose of the article is to study the methods of pelletizing control in the pelletizer drum and to assess of the moisturing quality in it.

## 2 Experimental programme

A study of the influence of humidity on the final particle size distribution of the charge and on the parameters of the layer was carried out at PJSC "MK "AZOVSTAL" [3]. Length of the drum

pelletizer -6 m, diameter -2.5 m, the angle of the axis  $-0^{\circ}$ , productivity -220 tons / hour. The current water consumption for moisture was  $6.5 m^3/hour$ . The moisture content W of the charge was increased from 4.48 to 8.3 - 9.1 %, the equivalent diameter  $d_e$  - from 1.04 to 3.5 - 4.2 mm. The variation of size V is decreased from 2.75 to 0.52 - 0.62 mm / mm.

The transit time of materials through the pelletizer and intermediate bunker was 75 sec. A heating of the charge by the heat of hot returned agglomerate allowed raising the temperature of the pelletized charge to 65 °C. In the course of studies, the water consumption for pelletizing of the charge was increased in comparison with the established service personnel by  $0.5 m^3/hour$  ( $\Delta W = 0.35$  %). The equivalent diameter  $d_e$  and the coefficient of variation V of the particle size of the granules of the pelletized sinter charge was determined by mid-logarithmic formulas [4, 5]. The measured parameters depend on many probabilistic factors, so it is not possible to stabilize them at the same value at the initial time. The equivalent diameter values were determined for the samples by sieving. The porosity was determined using a grid mathematical model based on the known fractional composition. Curves of change of the layer porosity, humidity of pelletized charge, pellets equivalent diameter and coefficient of variation, are presents by **Fig. 1**. The curves are obtained by the area method for the models presented below.



Fig. 1 Dynamics of changes in porosity (●), humidity (♦), equivalent diameter of particles (■) and coefficient of variation (▲) pelletized charge with the increase in water flow

It was found that when the changing humidity is from 8.3 to 9.9 % the value of the layer porosity is varies growing from 28 to 45 %, the mid-logarithmic diameter of granules – from 3.9 to 5.5 mm, the variation of size – from 0.35 to 0.57. Porosity and mid-logarithmic diameter of the granules increased and variation decreased when you add the humidity. This indicates low humidity of the pelletized charge. Due to the fact that the transition processes were investigated, the pelletizing parameters did not have a steady value and the humidity value, which corresponds to the maximum porosity of the layer, cannot be claimed.

The value of the coefficient of linear correlation between the layer porosity and the coefficient of size variation was R = -0.62. That is, the correlation is not high. This is due to the fact that the value of porosity depends on the deviation of small fractions relative to the dominant one, and the variation characterizes the deviation relative to the equivalent diameter. The values of the
dominant fraction and the equivalent diameter of the granules for bulk materials do not coincide. The correlation coefficient is negative because the size variation and the porosity change in inverse relationship  $\varepsilon = f(1/V)$ .

Based on measured data, it was found that with an increase in the water flow rate in pelletizer, the humidity of the charge at the outlet of the intermediate hopper of the loading device is stabilized within  $\tau_W = 150 - 200$  s and increases by 0.35 %<sub>abs</sub>. The delay time was  $\approx 30$  s.

It is necessary  $\tau_{\varepsilon}= 250 - 300$  s to stabilize the equivalent particle diameter, layer porosity and coefficient of variation. The equivalent diameter is increased by  $\approx 1.5 \text{ mm}$ , porosity – by 5.5 %<sub>abs</sub>, coefficient of variation – by 0.06. The delay time is the same for all three of these parameters and is  $\approx 60 \text{ s}$ . Time lag of stabilization of new values of porosity, equivalent diameter of granules and coefficient of variation from humidity  $\Delta \tau = \tau_{\varepsilon} - \tau_W = 100 \text{ s}$ , probably due to the following.

According to research Korotich V. I. a characteristic feature of the motion of the charge in the mode of rolling is the formation of "bud" around which the rotation of material occurs [6]. Experiments have shown that the material is segregated by size when moving: small fractions are concentrated near this point. Crumbling material moves in layers of thickness, which is equal to the average diameter of the granules. Thus, the first portions of water are transported to the pelletizer discharge end by large fractions faster than the mass transfer of small particles from the buds middle occurs. The phenomenon of the uneven distribution of water when the cost change is also confirmed by other researchers, who found that for pulsating water flow in pelletizer observed delamination of the granules.

## **3** Discussion of results

The aperiodic (inertial) first-order equation with lag to describe the transients of the drum pelletizer made [7]

$$W(p) = \frac{K_{ob}}{T_{ob}p + 1} \cdot e^{-p\tau_{lag}}; \ h(t) = K_{ob} \cdot \left(1 - e^{-\frac{t}{T_{ob}}}\right) \cdot 1\left(t - \tau_{lag}\right).$$
(1.)

where: W(p) – transfer function

p – Laplace operator  $K_{ob}$  – the gain  $T_{ob}[s^{-1}]$  – the time constant  $\tau_{lag}[s]$  – the lagging time h(t) – the equation of the curve of acceleration t[s] – the time  $1(t - \tau_{lag})$  - single function with delay

Dynamic parameters of the pelletizer drum were determined by the area method (**Table 1**) [8]. Indices at coefficients in **Table 1** correspond to the transfer functions (1) of the output moisture of the charge W, of the layer porosity  $\varepsilon$ , of the equivalent diameter of the granules  $d_e$  and of the coefficient of variation V from the water flow to the pelletizer.

	$K_{ob}$	$T_{ob}, s^{-1}$	$ au_{lag}, s$
Humidity W, %	$K_W = 42.17 \ \%/(m^3/s)$	$T_W = 46.50$	$\tau_W = 30$
Porosity $\varepsilon$ , %	$K_{\varepsilon} = 662.65 \ 1/(m^3/s)$	$T_{\varepsilon} = 88.20$	$\tau_{\varepsilon} = 60$
Equivalent diameter $d_e$ , mm	$K_d = 180.72 \ mm \ / \ (m^3/s)$	$T_d = 121.95$	$\tau_d = 60$
Size variation V, mm / mm	$K_V = -7.23 \ 1/(m^3/s)$	$T_V = 89.4$	$\tau_V = 60$

 Table 1 Characteristics of the drum-pelletizer

DOI 10.12776/ams.v25i1.1154

Gain factors are overestimated due to the fact that the water flow rate is specified in the SI system. For more production-specific units, their values must be divided by 3600 s. In addition, given the extreme nature of the change in porosity and in the equivalent diameter from the moisture content of the pelletized charge, the transfer coefficients of the object will have different values, depending on the properties of the charge and other parameters. Therefore, the effect of moisture on the layer should be considered in a small range. Changes in the transmission coefficients depending on the properties of the charge and humidity must be taken into account when controlling.

Note that the values of the constant time for porosity and variation of size isequal, which indicates their high correlation.

Also, despite the growth of the equivalent diameter, the size variation and porosity of the layer stabilize faster, which is explained by the narrowing of the range of granules diameters. Based on the values of time constants, the size variation stabilizes slightly longer.

A more accurate description of transition processes to calculate the right values of indicator of the quality of hydration necessary. Use of other laws changes is possible [7]:

• aperiodic (inertial) link of the second order with delay

$$W(p) = \frac{K_{ob}}{(T_3 p + 1)(T_4 p + 1)} \cdot e^{-p\tau_{lag}}, \ h(t) = K_{ob} \cdot \left[ 1 - \frac{1}{T_3 - T_4} \left( T_3 e^{-\frac{t}{T_3}} - T_4 e^{-\frac{t}{T_4}} \right) \right] \cdot 1\left(t - \tau_{lag}\right);$$
(2.)

where:  $T_3$  and  $T_4[s^{-1}]$  – the time constant

• oscillating link with an additional component with delay

$$W(p) = \frac{K_{ob}}{p(T^2 p^2 + 2T\xi p + 1)} \cdot e^{-p\tau_{lag}}, \ h(t) = K_{ob} \cdot \left[1 - Ce^{-\gamma t}\sin(\lambda t + \theta)\right] \cdot 1(t - \tau_{lag}),$$
(3.)

where: 
$$0 \le \xi \le 1$$
;  $C = \frac{1}{\lambda T}$ ;  $\theta = \operatorname{arctg} \frac{\lambda}{\gamma}$ ;  $\gamma = \frac{\xi}{T}$ ;  $\lambda = \frac{\sqrt{1-\xi^2}}{T}$ .

The calculated values of the coefficients of the formula (3) are shown in Table 2.

	The curve parameters of acceleration							
	W	$d_e$	3	V				
T =	60.24	69.22	57.03	57.47				
ξ=	0.39	0.88	0.77	0.78				
C =	1.08	2.11	1.58	1.59				
$\lambda =$	0.0153	0.0068	0.0111	0.0109				
$\gamma =$	0.0064	0.0127	0.0136	0.0135				
$\theta =$	1.17	0.49	0.69	0.68				

Table 2 Values of pelletizer model (3) coefficients

The settings of the PI controller corresponding to the degree of oscillation m = 0.351 for control using various controlled input parameters are determined by the method of extended frequency response (**Table 3**).

Para- meter	Regulator**		Control quality											
	K <sub>p</sub> ·10 <sup>-3</sup>	$T_i \cdot 10^{-4}, s^{-1}$	Overshoot, %			<b>Regulation time, s</b>			Maximum deviation					
			W de		ε ν						W	d.	8	<i>V</i> ,
				$d_e$		W	$d_e$	3	V	%	mm	%	<u>mm</u>	
											/0		, •	mm
W	1.5	4.5	20.0	16.0	18.6	18.7	670	885	680	680	0.030	0.8	3.5	-0.38
$d_e$	0.17	0.16	22.0	20.0	21.7	21.5	1230	1450	1300	1300	0.036	1.1	4.6	-0.50
З	1	0.54	20.8	18.1	20.0	19.7	1400	1600	1450	1450	0.036	1.14	4.6	-0.52
$V^*$	12.5	13.6	20.8	17.8	19.3	20.0	1300	1600	1270	1270	0.036	1.13	4.7	-0.51

**Table 3** Results of the regulation of the controlled parameters

\* - with positive feedback

\*\* -  $K_p$ ,  $T_i$  - the proportional and integral setting

Quality indicators of regulation of the pelletizer drum for each controlled parameter are investigated (**Table 3** and **Fig. 2**). The settings of the PI-controller corresponding to 20 % overshoot of each of the parameters were consistently set and controlled changes in the remaining parameters. Based on this, we determined the quality of transients for them.

From the research results it follows that the overregulation changes insignificantly for all variants. However, the humidity control of the charge at the outlet of the pelletizer has the best characteristics. At the same time, the duration of the transition process and deviations of all parameters are the smallest. This control is the most optimal for stable raw charge materials. Nevertheless, the humidity at the fluctuating initial dosing and fractional composition of the charge should provide maximum gas permeability. In addition, the measurement error is affected by hydrated moisture. Therefore, the porosity of the layer, the equivalent diameter of the granules and the variation of their size to regulate and find the maximum gas permeability are more preferred. They are also more closely related to the productivity of the agglomeration process.



Fig. 2 Transients in the control of humidity of the pelletized charge (a) and porosity of the formed layer (b)

It is found that the regulation of the equivalent diameter of the granules has insignificantly better regulation. But given the fact that the maximum equivalent diameter corresponds to the formation of waterlogging, it is necessary to take into account all three parameters in the interaction [9-11].

The effective length of the pelletizer drum, on which the most intensive growth of granule size occurs, depends on the parameters of the shower unit inside. Typically, the moistening is carried out on 1/3 of the length of the pelletizer from the entrance. Based on the fact that the moisture content of the charge at the outlet is changing much faster than the porosity of the layer, the variation in size and, especially, the equivalent diameter, it follows that the method of supplying moisture to the charge requires improvement.

The relative difference  $\Delta S$  between the areas above the normalized curves of acceleration of humidity  $S_W$  and equivalent diameter  $S_d$  (or porosity  $S_{\varepsilon}$ ) to assess the quality of moisturing can be used (**Fig. 3**)

$$K_y = \frac{S_d - S_W}{S_W} \,. \tag{4.}$$



**Fig. 3** Explanation of the formula (4)

The proposed coefficient shows the deviation of the acceleration curves by the parameters of the layer and the fractional composition of the charge relative to the base acceleration curve by humidity. Inefficient moisturizing corresponds to the irrational distribution of water on the surface of the material inside the pelletizer. More intensive mass transfer of lumpy fractions under the action of hygroscopic adhesion forces corresponds to the zero value of the index  $K_y$ . For an aperiodic (inertial) link (1), the area above the acceleration curve h(t) is

$$S = \int_{0}^{\infty} (1 - h(t)) dt = \int_{0}^{\infty} e^{-\frac{t}{T_{ob}}} dt = T_{ob} e^{-\frac{t}{T_{ob}}} |_{0}^{\infty} = T_{ob} .$$
(5.)

Taking into account the lag time  $S = T_{ob} + \tau_{lag}$ . Accordingly, the indicator  $K_y$  by the equivalent diameter is equal to

$$K_{y} = \left(T_{d} + \tau_{d} - T_{W} - \tau_{W}\right) / \left(T_{W} + \tau_{W}\right).$$
(6.)

Similarly, for the model of the drum (2)

$$S = \int_{0}^{\infty} \frac{1}{T_{3} - T_{4}} \left( T_{3} e^{-\frac{t}{T_{3}}} - T_{4} e^{-\frac{t}{T_{4}}} \right) dt = T_{3} + T_{4}$$
(7.)

and given the time lag  $S = T_3 + T_4 + \tau_{3an}$ . Then

DOI 10.12776/ams.v25i1.1154

p-ISSN 1335-1532 e-ISSN 1338-1156

$$K_{y} = \frac{T_{3d} + T_{4d} + \tau_{d} - T_{3W} - T_{4W} - \tau_{W}}{T_{3W} + T_{4W} + \tau_{W}} \,. \tag{8.}$$

For the model (3)

$$S = \int_{0}^{\infty} C e^{-\gamma t} \sin\left(\lambda t + \theta\right) dt = C \frac{\lambda \cdot \cos\left(\theta\right) + \gamma \cdot \sin\left(\theta\right)}{\gamma^{2} + \lambda^{2}}.$$
(9.)

 $K_y$  is determined after substitution of the corresponding values of the areas calculated by the formula (9).

The value of the index  $K_y$  at the same time step of measurements of humidity  $W_i$  and equivalent diameter  $d_i$  (porosity  $\varepsilon_i$ , variations of size  $V_i$ ) can be determined approximately on the basis of the trapezoid method [12]

$$S = n - \left(\frac{h_0 + h_n}{2} + \sum_{i=1}^{n-1} h_i\right),$$
(10.)

where: n – the number of the last dimension, starting from 0.

The values  $K_y$  calculated by different methods are presented in **Table 4**.

**Table 4** Values of the index  $K_y$ 

Link type			$K_y$			
			3	V		
Aperiodic (inertial) link of the first order with lag			0.94	0.95		
Oscillatory link with additional and-component with lag			0.94	0.95		
The method of transpos	Value	1.47	1.01	1.03		
The method of trapezes	Error *, %	6.73	7.86	7.85		

\* - the true value of the  $K_y$  corresponds to the oscillatory link with an additional I-component with a lag

It follows that the trapezoid method allows estimating the moisturing parameters with a satisfactory error.

## 4 Conclusion

The quality of the charge pelletizing in the drum depends to a significant extent on the correspondence of the water mass transfer rates and fine solid particles between the granules. The lagging to 30 s behind the rate of change of the equivalent diameter of the granules, the porosity of the layer and the variation of size from humidity is observed. The mismatch of these speeds reduces the effective length of the pelletizer drum. The coefficient characterizing the shower unit was developed. Its value for the industrial drum is 0.94 - 1.38 depending on the compared parameters. The minimum value of which increases the effective length of the pelletizer by 3 m.

## References

[1] E. W. Voice, R. Wild: J. Metals, 1958, No. 2, p. 105-110

- [2] Sheng-li Wu, Juan Zhu, Ji-cheng Bei, Guo-liang Zhang, Xiao-bo Zhai: International Journal of Minerals, Metallurgy and Materials, Vol. 22, No 9, 2015, p. 907-915, DOI: 10.1007/s12613-015-1149-0
- [3] S. V. Krivenko: Metallurgical processes and equipment: International scientific-technical and production journal, 2011, No 2(14), p. 22-26
- [4] S. G. Bratchikov, Y. L. Berman, J. L. Belotcerkovsky: *Thermotechnics of iron ore sintering*, Moscow, 1970
- [5] S. V. Krivenko: News of Higher educational institutions. Ferrous metallurgy: Scientific, technical and production journal, 2010, No. 8, p. 7-11
- [6] V. I. Korotych, Yu. A. Frolov, G. N. Bezdezhsky: Agglomeration of ore materials, Yekaterinburg, 2003
- [7] I. M. Makarov, I. M. Mensky: Linear automatic systems (theory elements, calculation methods and reference material), second ed., Moscow, 1982
- [8] Kh. Guretskiy: Analysis and synthesis of control systems with delay, Moscow, 1974
- [9] S. V. Krivenko: Metal and casting of Ukraine: Scientific journal, 2011, No. 8, p. 25-29
- [10] P. Kapur: International Journal of Mineral Processing, 2003, No 72, p. 417-427, DOI: 10.1016/S0301-7516(03)00116-9
- [11] Yu. A. Frolov: Stal, 2009, No. 8, p. 2–7. DOI:10.3103/S0967091209080099
- [12] Atkinson, Kendall E.: An Introduction to Numerical Analysis, second ed., New York, 1989

## Acknowledgements

The article is made in cooperation with the Department of iron metallurgy of Pryazovskyi State Technical University (Mariupol, Ukraine).