Mössbauer study of steels cooled to dry ice temperature

B.S. Boyanov¹, D.G. Paneva² and K.I. Ivanov³

¹Plovdiv University “Paisii Hilendarski”, 24 Tsar Assen St., 4000 Plovdiv, Bulgaria
²Institute of Catalysis, Bulgarian Academy of Science, 1113 Sofia, Bulgaria
³Agricultural University, Department of Chemistry, 12 Mendeleev St., 4000 Plovdiv, Bulgaria

E-mail: boyanb@uni-plovdiv.bg

Abstract. Based on the change of hardness $H_b$, the parameter $\beta$, the microstructure and Mössbauer spectra of 7 kinds of steels the conclusion is made that in the conditions of CO$_2$ (dry ice) cleaning, using dry ice for repair and modification of pipes and dry snow for cooling (-78.3 °C) no significant change in the mechanical properties of the cleaned surfaces, mechanically processed steels and the steel pipes can be expected.

1. Introduction
CO$_2$/dry ice cleaning is effectively used in wide ranges of application – from slag removal to cleaning delicate semi-conductors and complicated electrical chips. This method allows for direct use (on-line) with no damage to the cleaned equipment [1].

The essence of the method for quick repair and modification of pipes with “Qwikfreezer” is in obtaining two ice “plugs” on both sides of the section of the pipe that will be repaired or modified. This can be done by quick freezing using carbon dioxide and using the developed system for quick freezing [2].

A new technology is developed to use solid CO$_2$ to cool and grease the processed metal surfaces as well as removal of the cut waste elements. This technology is called “snow machining” and one day it could eliminate the use of petrol or synthetic chemical fluids for metal cutting and cleaning metal parts in industry [3]. Very important in terms of using CO$_2$/dry ice particles are the consequences of thermal shock on the cleaned or cooled material. In this connection the main objective of the current study is to check the influence of cooling to the temperature of dry ice (-78.3 °C) on the microstructure and Mössbauer spectra of various types of steels and their hardness.

2. Experimental
Objects of study are 7 kinds of steels - C10, C45, C20Ch, 65G, U8A, Ch12, SchCh15 - (Table 1).

Based on the measurement of hardness an assessment can be made for the resistance to cold of the steels using a comparatively simple and repeatable methodic. It consists of measuring hardness at a room temperature $H_r$ and comparing with the hardness at the low temperature $H_t$, during which the parameter $\beta$ is calculated [4]:

$$\beta = \frac{H_t}{H_r}$$  \hspace{1cm} (1)
The higher the value of the parameter $\beta$, the more susceptible the metal is to crumbling under the effect of cold.

Mössbauer spectra (MS) were obtained at room temperature (RT) with a Wissel electromechanical spectrometer (Wissenschaftliche Elektronik GmbH, Germany) working at a constant acceleration mode. A $^{57}$Co/Cr (activity $\equiv$ 45 mCi) source and an $\alpha$-Fe foil standard were used. The experimentally obtained spectra were treated using the least squares method. The parameters of hyperfine interaction such as isomer shift ($\delta$), quadrupole splitting ($\Delta$) and effective internal magnetic field (B) as well as the line widths ($\Gamma$) and the relative area (G) of the partial components of the spectra were determined. The areas of the observed signals have been used to evaluate the relative populations of the different iron species, assuming an equal free recoil fraction for all species.

Table 1. Chemical composition of the studied steels, %

| Type of steel | C    | Mn    | Si    | Cr    | Ni    | P    | S    |
|--------------|------|-------|-------|-------|-------|------|------|
| C10          | 0.07 – 0.14 | 0.17 – 0.37 | 0.35 – 0.65 | 0.035 | 0.04 | -    | -    |
| C45          | 0.42 – 0.50 | 0.50 – 0.80 | 0.17 – 0.37 | 0.25  | 0.25  | 0.040 | 0.040 |
| C20Ch        | 0.17 – 0.23 | 0.60 – 0.90 | 0.17 – 0.37 | 0.70 – 1.0 | -    | -    | -    |
| 65G          | 0.62 – 0.70 | 0.90 – 1.20 | 0.17 – 0.37 | 0.25  | 0.25  | 0.040 | 0.040 |
| U8A          | 0.76 – 0.83 | 0.17 – 0.28 | 0.17 – 0.33 | 0.2   | 0.2   | 0.025 | 0.018 |
| Ch12         | 2.00 – 2.20 | 0.15 – 0.45 | 0.10 – 0.40 | 11.5 – 13.0 | 0.35  | 0.030 | 0.030 |
| SchCh15      | 0.95 – 1.05 | 0.20 – 0.40 | 0.17 – 0.37 | 1.3 – 1.65 | 0.3   | 0.027 | 0.020 |

3. Results and discussion
The obtained results about the phases and the structural phases of the samples are shown in Table 2.

After cooling for the duration of 24 h at the temperature of dry ice the observed microstructure, shown in Table 2, is preserved. Based on the obtained results and the microphotographs it is confirmed that the cooling at the temperature of dry ice for a duration significantly greater than the duration of influence of the blasting stream from the blasting machine upon the cleaned material, and the time necessary for the repair and modification of pipes does not influence to a measurable degree the microstructure of the studied steels. An insignificant decrease of the size of grains is observed with C10, C45 and C20Ch.

Table 2. Results from the microstructure analysis of the studied steels

| Samples | Microstructure |
|---------|----------------|
| C10     | Ferrite + perlite, with ferrite grain size 7-8 (6) grade and Widmanstätten pattern of 1.5 grade |
| C45     | Perlite + broken ferrite net. Size of perlite grain ~7-6-8, single 5 grade and Widmanstätten pattern up to 1.5 grade |
| C20Ch   | Ferrite + perlite, with ferrite grain size ~8-7 (6) grade with axial disalignment and Widmanstätten pattern of 1 grade |
| 65G     | Perlite with different dispersity + ferrite |
| U8A     | Troostite |
| Ch12    | Sorbitic perlite + carbides |
| SchCh15 | Sorbite, with small amount of fine carbides |

The steels studied for the influence of low temperature treatment on their strength are also subjected to a study of their hardness with the Brinell method. For the studied steel samples the parameter $\beta$ is
calculated [4]. The obtained results show that the cooling of up to -78.3 °C influences the hardness of samples insignificantly. The observed increase is measured with values that do not give reason to reach the conclusion that at the processing of pieces and items with dry ice their mechanical properties can be changed to such a degree that irreversible changes take place in their hardness and entirety. The model of the Mössbauer spectra processing (Figure 1) for each sample before and after cooling 24 h at -78.3 °C is the same.

The accepted in literature [5] designations of ferrite 1 and ferrite 2 are used in the processing of analogical Mössbauer spectra with more than 1 sextet. According to the degree of deviation of the components spectral lines with superfine structure from the theoretical Lorentians either 2 or 3 sextets are introduced. All mathematical processing of the spectra includes components designated as Ferrite 1 and Ferrite 2 (see bar-diagram above the spectra in Figure 1) with different ratio for the different samples. The component Ferrite 1 has approximately the same hyperfine parameters as the α-Fe and it is result of the presence of rich-iron ferrite phase. The value of B is in the range 33-33.3T for all 14 samples. The hyperfine field in some samples is 1% larger than that of the iron field (B = 33T) and is probably related to the plastically-deformed structure accompanying rolling. The second component Ferrite 2 has lower values of B=30.5 - 31.5T compared to the α-Fe, which can be explained with the inclusion of solute atoms on substitutional sites in iron lattice such as Cr, Ni and Mn. Samples C10, C45, C20Ch, 65G, U8A, Ch12, and SchCh15,24h are shown in the figure.
C45, C20Ch, 65G consist of 2 magnetic components only - Ferrite 1 and Ferrite 2. Relative content of these components are 90/10, 83/17, 80/20, 78/22%, respectively. The analysis of Mössbauer spectra of the pair of samples (before and after cooling at -78.3°C) shows the equal values in range of error 1%.

A new sextet component (9%) is introduced in the processing of the spectra of steel U8A and U8A, 24h samples except components Ferrite 1 and Ferrite 2. The parameters (δ=0.18 mm/s, Δ=0.04 T) of new component allow identification of carbide phase Fe3C – cementite. Ratio of Ferrite 1 and Ferrite 2 is 71%/20% of sample before cooling and it changes to 73%/18%.

A doublet component with the designation of (Fe,Cr)3C is included for SchCh15 (SchCh15, 24h) and Ch12 (Ch12, 24h). The main components are magnetic - Ferrite 1 and Ferrite 2. The doublet parameters (δ=0.15-0.17 mm/s Δ=0.52- 0.54 mm/s) are close in the two spectra, and its content is different in the two pairs of samples – it is 14 and 13% respectively for the pair Ch12/(Ch12, 24h). Relative content of paramagnetic components in the pair SchCh15/(SchCh15, 24h) is 11 and 10%. It is visible that these samples have the greatest chrome content (Table 1). The determined isomer shift is close to that of the cementite, and can be said that the doublet is connected with a carbide phase or other similar to carbide. It is presented by a doublet [6] because of the inclusion of ions other than iron (for example chrome) and collapse of hyperfine magnetic interactions. As much as this component is not registered in the spectra of the other samples where the chrome content is far lower, we connect this component with phase (Fe,Cr)3C. This designation must be considered as conditional and as one possibility to explain the registered doublet component in these two spectra. It is possible that other admixture atoms are included in this carbide phase.

The comparison of the parameters for the samples before and after 24 h treatment at -78.3 °C and the presented data show insignificant deviation in their values.

All obtained results from the detailed study of steels with the help of Mössbauer spectroscopy give reason for the conclusion that treatment at low temperatures (-78.3 °C) for the duration of up to 24 h does not lead to essential changes in the microstructure of the samples.

4. Conclusions
1. The data from the Mössbauer spectroscopy for the initial steels and the steels cooled for 24 hours at the temperature of dry ice (-78.3 °C) show that the microstructure of the separate specimens (initial and cooled) does not change measurably due to the cooling.
2. Based on the change of Mössbauer spectra, H0, the parameter β, and the microstructure of the steels, it can be concluded that at conditions of cleaning with CO2 (dry ice), using dry ice for repair and modification of pipes and for replacement of lubricants (during cutting, grinding, drilling, etc.), a significant change in the mechanical properties of the cleaned surfaces, the steel pipes and mechanically processed steels cannot be expected.

Acknowledgement: The studies are carried out through project IF-02-1402/2006, financed by the National Innovation Fund, in which the Plovdiv University Paisii Hilendarski is a Partner.

References
[1]. Spur G, Uhlmann E, Elbing F 1999 *Dry-ice blasting for cleaning: process, optimization and application, Wear*, 233-235, pp 402-411
[2] http://www.QwikFreezer.com
[3]. Process news: Snow-machining cuts out lubricants 2005 *Chemical Engineer* 767, 17
[4]. Matyunin V M *Operative diagnostics of mechanical properties of constructive materials*, Publishing House MEI, Moscow, 2006, p.214 (in Russian).
[5] Hanc A, Binczyk F 2008 *Archives of Materials Science and Engineering*, 31 101-104
[6] Oztürk Ö, Onmuş O, Williamson D L 2005 *Surf. Coat. Technol.* 196 341– 348

IOP Publishing
Journal of Physics: Conference Series 217 (2010) 012074 doi:10.1088/1742-6596/217/1/012074