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THE MÖOSSABAUER SPECTROSCOPY STUDIES OF ε CARBIDES PRECIPITATION

BADANIA WYDZIELEŃ WĘGLIKA ε PRZY UŻYCIU SPEKTROSKOPII MÖSSBAUEROWSKIEJ

This work complements the knowledge concerning the kinetics of ε carbide precipitation and decomposition. Investigations were performed on 120MnCrMoV8-6-4-2 steel, which was designed in 1998, in Phase Transformations Research Group of Department of Physical and Powder Metallurgy at the Faculty of Metals Engineering and Industrial Computer Science at AGH University of Science and Technology in Krakow. The samples of investigated steel were austenitized at the temperature of 900°C and hardened in oil. Next, three from four samples were tempered. Tempering consisted of heating the samples up to chosen temperatures with a heating rate of 0.05°C/s and, after reaching desired temperature, fast cooling. CEMS technique was applied for Mössbauer studies.

Stabilized retained austenite by heating up to 80°C, in the result of mechanical destabilization, transforms into low-temperature tempered martensite, with the microstructure of low bainite (into the structural constituent in which ε carbide exists). Influence of hardened steel heating temperature on ε carbide precipitation was determined. Also the knowledge of the mechanisms of precipitation and decomposition of ε carbide enables proper design of the heat treatment of 120MnCrMoV8-6-4-2 steel in respect to its application for hot working tools.

Mössbauer spectroscopy was applied not only for quantitative analysis of ε carbide, but also to analyze the values of hyperfine magnetic field, quadrupole splitting, isomeric shift and relation of 2 to 3 Zeeman splitting component line, what resulted in significant conclusions concerning the changes in its morphology and the level of stresses being present in it.

Keywords: mössbauer spectroscopy CEMS, tool steel, tempering, ε carbides

W pracy przedstawiono wyniki pomiarów mössbauerowskich wykonanych na odpuszczonych do wybranych temperatur wcześniej zahartowanych próbkach ze stali 120MnCrMoV8-6-4-2. Pomiary wykonywano zarówno na powierzchniach szlifowanych jak i wypolerowanych po szlifowaniu. Poszczególne składowe widma mössbauerowskiego zostały zidentyfikowane i przypisane odpowiednim fazom. W pracy skupiono się na analizie składowych pochodzących od węglika ε.

Do pomiarów mössbauerowskich zastosowano technikę elektronów konwersji wewnętrznej CEMS z detektorem gazowym, wypełnionym objętościowo 98% He + 2% Ar, pod ciśnieniem 0,9 at. Źródłem mössbauerowskim był ^{57}CoRh o aktywności 10 mCi. Zastosowanie techniki CEMS pozwoliło na badanie warstw powierzchniowych o grubości około 100 nm. Parametry widm składowych zostały wyznaczone w oparciu o program filtrujący MOSDS.

Na podstawie analizy nadsubtelnego pola magnetycznego, rozszczepienia kwadrupolowego, przesunięcia izomerycznego, stosunku 2 do 3 linii sekstetu zemanowskiego oraz intensywności widma składowego pochodzącego od węglików ε wnioskowano na temat produktów destabilizacji austenitu szczątkowego po odpuszczeniu ciągłym do 80°C, o wpływie tekstury osnowy na orientację krystalograficzną wydzieleń węglika ε, zakresie temperatur występowania węglików ε w strukturze podczas ciągłego odpuszczania oraz przemianie ε – cementyt.

Otrzymane wyniki pozwolą w przyszłych publikacjach na dyskusję, która uzupełni wiedzę na temat kinetyki przemian fazowych przy odpuszczaniu stali stopowych.

1. Introduction

Application of dilatometric, magnetic, X-ray, and microscopic analysis gives a lot of useful information about the kinetics of precipitation and decomposition of transition carbides in steels [1-8]. Mössbauer spectroscopy enables confirmation of results obtained from mentioned above techniques, as well as gives additional data [9-21]. Significant experimented difficulties can be met in the case of the analysis of transition carbides,

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including ε carbide. The reason for these difficulties is that this carbide occurs in the structure only when the steel matrix consists of strongly deformed martensite. In such cases Mössbauer spectroscopy can help to confirm whether ε carbide or other transition carbides are present in the structure.

This work presents the results of investigations using Mössbauer spectroscopy technique and their interpretation concerning ε carbide and its transformation during tempering in relation to previously conducted dilatometric, microscopic and mechanical investigations [1].

2. Tested material

The research was conducted on a new high-carbon alloy steel with the chemical composition given in Table 1.

TABLE 1

Chemical composition of the investigated steel

mass %								
C	Mn	Si	P	S	Cr	Mo	V	Al
1.22	1.93	0.19	0.018	0.02	1.52	0.36	0.17	0.04

3. Experimental procedure

Samples, taken from investigated steel, were austenitized at the temperature of 900°C and hardened in oil. Austenitizing time was 20 minutes. After that three of four samples were tempered. Tempering consisted of heating the samples up to chosen temperatures at the heating rate of 0.05°C/s and fast cooling after reaching desired temperature.

Sample No. 1 was left in as-hardened state. After hardening, sample No. 2 was heated to 80°C, sample No. 3 was heated to 210°C and sample No. 4 was heated to 350°C. The temperatures up to which the investigated samples were heated were selected in order to enable the precipitation of ε carbide in sample No. 2 during tempering. Sample No. 3 was heated up to the temperature at which the precipitation of ε carbide was finished and cementite started to precipitate without transformation of retained austenite. The temperature, up to which the sample No. 4 was heated after hardening was selected as a temperature corresponding to the finish of transformation of retained austenite.

All the temperatures mentioned above were selected basing on CHT diagram published in work [22]. Figure 1 presents a dilatogram of test steel sample quenched from 900°C and subsequently heated at the rate of 0.05°C/s, along with corresponding differential curve.

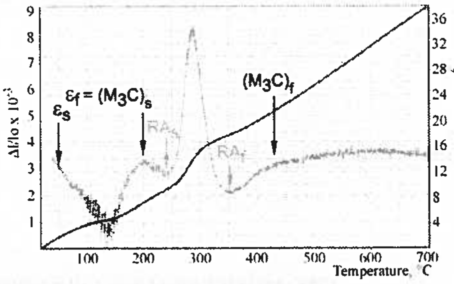

Fig. 1. Dilatogram recorded during heating the sample at the rate of 0.05°C/s, along with corresponding differential curve [1]. Sample was hardened from 900°C prior to heating

For the study a Conversion Electron Mössbauer Spectroscopy (CEMS) with gas detector, filled with 98% He + 2% Ar, under pressure of 0.9 at., was applied. A Mössbauer source was ^{57}CoRh of activity of 10 mCi. Application of CEMS technique allowed to investigate the surface layers of thickness of about 100 nm. Two sides of each sample were investigated, one was grinded only, while the other one was polished after grinding.

4. Research results and discussion

On the grounds of the results of the investigations using TEM [1] it is noticeable, that directly after hardening from 900°C the microstructure of studied steel consists of martensite, retained austenite and spheroidal particles of alloyed hypereutectoid cementite, undissolved during austenitizing. Obtained Mössbauer spectrums were presented by Krawczyk et. al. [23].

The analysis of the intensity of individual component spectra may be used for determination of the amount of phase constituents, and for the analysis of qualitative changes of the quantity of particular phase constituents during steel tempering in particular.

Basing on the analysis of hyperfine magnetic field and on previously performed investigations, conducted with different techniques [1,22], it is possible to determine which phase a particular spectrum comes from. The analysis of hyperfine magnetic field (Zeeman sextets) allowed to distinguish between component spectra coming from ^{57}Fe atoms existing in the structure of martensite (or ferrite in the case of higher tempering temperatures), in the structure of ε carbide, and in cementite, independently precipitated during tempering. A component spectrum was also identified, characterized by single peak (without quadrupole or Zeeman splitting) as corresponding to precipitations of alloyed hypereutectoid cementite (which is paramagnetic), undissolved during austenitizing. While component spectrum of quadrupole splitting coming from ^{57}Fe atoms located in the structure of retained austenite.

The values of hyperfine magnetic field on ^{57}Fe atomic nucleuses, determined for the third component of Mössbauer spectrum as regards its intensity, indicate that these are the components coming from ferromagnetic carbides. Big differences in hyperfine magnetic fields coming from Fe atoms existing in the structure of carbides, measured on samples tempered at the temperatures of 80°C and 210°C, from ^{57}Fe atoms from precipitated carbides during tempering at the temperature of 350°C, allow to state that these are the carbides of different crystal structure. Data from work [10] as well as the research on the products of phases transformations during tempering of this steel, performed with the use of other research methods [1] show that mentioned above spectrum components measured on the samples tempered at 80°C (polished surface) and at 210°C (ground and polished surface) come from ε ($Fe_{2,4}C$) carbide. However, component spectrums, obtained on the sample tempered at 350°C, come from ^{57}Fe atoms present in the structure of cementite [1,10,23]. Percent volume of the intensity of the component spectrum coming from ε carbides in relation to the tempering temperature is shown in Figure 2. The lack of simultaneous occurrence of spectrums from ε carbide and cementite may suggest independent nucleation of cementite in the structure of steel during its tempering.

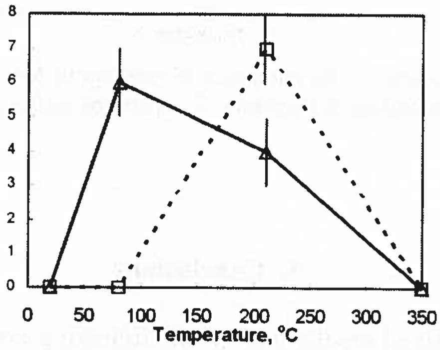

Fig. 2. Changes of intensity (S) of Mössbauer component spectrum corresponding to ε carbides: □ – polished surface, Δ – grinded surface

In the case of the sample tempered at 80°C the presence of component spectrum coming from ε carbide and measured only on the polished surface should be attributed to the mechanical destabilization of the part of retained austenite. The application of Mössbauer spectroscopy can give the information from thin layer of the surface of investigated sample. In a part of the volume of this layer, stresses resulting from polishing cause the mechanical destabilization of retained austenite. This problem was described in detail in work [9]. It can be noticed, that tempering of investigated steel at the temperature of 80°C causes the changes in the chemical composition of retained austenite (as compared with its chemical composition after hardening). These changes, causing the mechanical destabilization of retained austenite, lead to transformation of its part into supersaturated ferrite and ε carbides (the products of this transformation have the structure similar to that of lower bainite).

Moreover, such mechanical destabilization of retained austenite in hardened sample causes its transformation into martensite. The presence of component spectrum coming from ε carbide, both on ground and on polished surface of the sample tempered at 210°C, indicates that at this temperature ε carbide precipitated in martensite, what confirms the results of TEM investigation performed on the same material (Fig. 3).

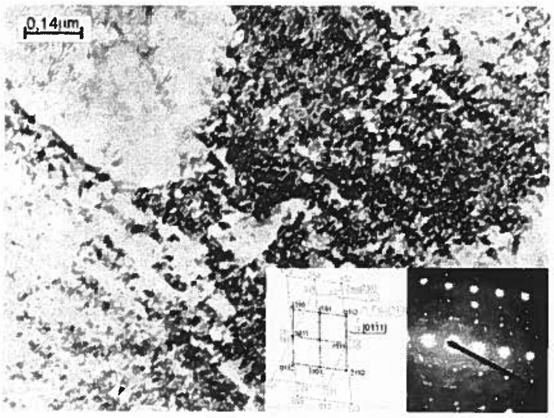

Fig. 3. Microstructure of steel hardened at 900°C and then tempered at 210°C at the rate of 0.05°C/s, observed in the area of the presence of ϵ carbide. Bright field TEM image along with diffraction pattern and its solution

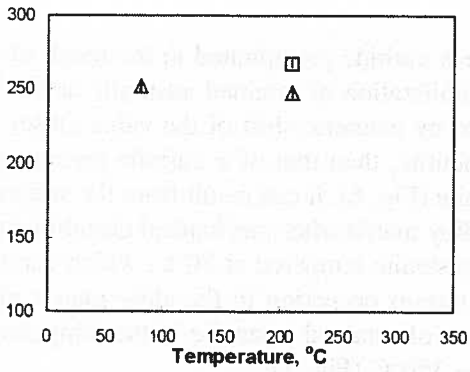

Fig. 4. Changes of hyperfine magnetic field (H) of Mössbauer component spectrum corresponding to ε carbides: □ – polished surface, Δ – grinded surface

Hyperfine magnetic field on ^{57}Fe atomic nucleuses, coming from ε carbide revealed on the surface layer of ground sample No. 3, is weaker than that measured on polished surface (Fig. 4). It may suggest, that ε carbide precipitating in martensite matrix is characterized by stronger hyperfine magnetic field on ^{57}Fe atomic nucleuses than carbide formed during mechanical destabilization of retained austenite. Moreover, comparing the hyperfine magnetic field coming from ε carbide on ground surfaces of the samples tempered at 80°C and 210°C one can notice, that in the result of the increase of tempering temperature, the chemical composition of mechanically destabilized retained austenite changes. This change results from the formation of ε carbide, characterized by weaker hyperfine magnetic field on ^{57}Fe atomic nucleuses, during the transformation of retained austenite tempered at higher temperature.

Precipitates of ε carbide is characterized by the small quadrupole splitting (Fig. 5). The biggest value of quadrupole splitting was noticed for ε carbide formed in the result of bainitic transformation during destabilization of retained austenite tempered at 210°C (ground surface of sample No. 3). It can be expected, that carbide formed that way is the most defected structure.

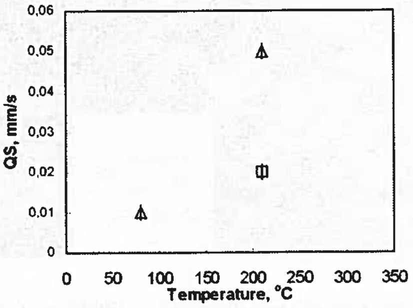

Fig. 5. Changes of quadrupole splitting (QS) of Mössbauer component spectrum corresponding to ϵ carbides: □ – polished surface, Δ – grinded surface

The ε carbide precipitated in the result of mechanical destabilization of retained austenite at 80°C is characterized by isomeric shift of the value closer to that of the cementite, than that of ε carbide precipitating from martensite (Fig. 6). It can result from the stresses formed in the alloy matrix after mechanical destabilization of retained austenite tempered at 80°C, which can be similar to the stresses occurring in the alloy matrix after transformation of retained austenite in the temperature range of 240 ÷ 350°C (Fig. 1).

The values of A2 parameter (intensity of the component line No. 2 to the component line No. 3 ratio in Zeeman spectrums) in the case of ^{57}Fe atoms present in the structure of ε carbide in comparison with such parameter for cementite revealed after tempering (at 350°C) of hardened sample may indicate, that ε carbide forms more in the result of oriented nucleation than it happens in the case of cementite (Fig. 7). It most probably results from the fact, that ε carbide nucleates inside martensite layers, while cementite nucleates on the boundaries of these layers or on the grain boundaries. This is the next proof that the transformation of ε into M_3C proceeds by independent nucleation.

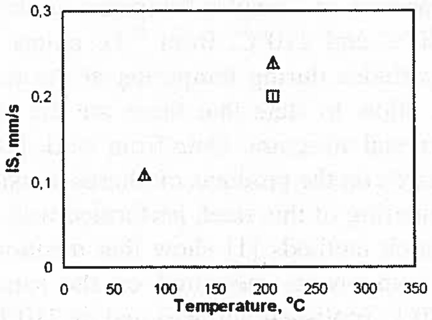

Fig. 6. Changes of isomeric shift (IS) of Mössbauer component spectrum corresponding to ε carbides: □ – polished surface, Δ – grinded surface

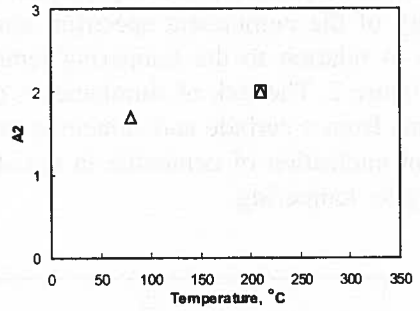

Fig. 7. Changes of A2 parameter of component Mössbauer spectrum corresponding to ε carbides: □ – polished surface, Δ – grinded surface

5. Conclusions

Obtained results lead to the following conclusions:

- stabilized by heating up to 80°C retained austenite undergoes, in the result of mechanical destabilization, transformation into low-temperature tempered martensite of the structure of low bainite, in which ε carbide exists,
- ε carbide precipitates during tempering of investigated steel,
- transformation of ε carbide into cementite proceeds by independent nucleation,
- heating up to 350°C of investigated steel causes complete dissolution of previously precipitated ε carbide,
- Mössbauer spectroscopy enables investigating transformations of transition carbides during tempering of investigated steel.

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