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Experiments on Obtaining Silicified Welded Joints Using Mechanical Vibrations

Bogdan NOVAC
"Ovidius" University of Constanța, Romania, bogdannovac@yahoo.com

Abstract
The paper presents the possibility of improving the mechanical properties, of welded parts, subjected to thermochemical silicification treatment. The silicification process depends very much on the carbon content of the silicify welding steel. The silicate layer has a ferrite structure alloyed with silicon. At higher concentrations in silicon, is formed the cementite alloyed with silicon and silicon carbide. This is the reason why it is recommended that low carbon steels should be used for silicification. The chemical reactions in the presence of silicon are complicated and they are depending on the value of the free enthalpy. For this purpose, a program was developed, which allows a quick appreciation of the reaction possibilities, based on thermodynamic calculations. The program can also test, chemical reactions for nitriding and carbonitriding. The welded parts subjected to the silicification treatment have a lower thermally influenced area and lower internal stresses. It has been shown that silicification also improves the protective properties of the surfaces of welded joints in order to eliminate the corrosion process in various corrosion environments. The silicate joint no longer needs to be galvanically coated to withstand corrosive environments.

Keywords
silicate layer, welded joints, microstructure, diffusion speed, carbon steels

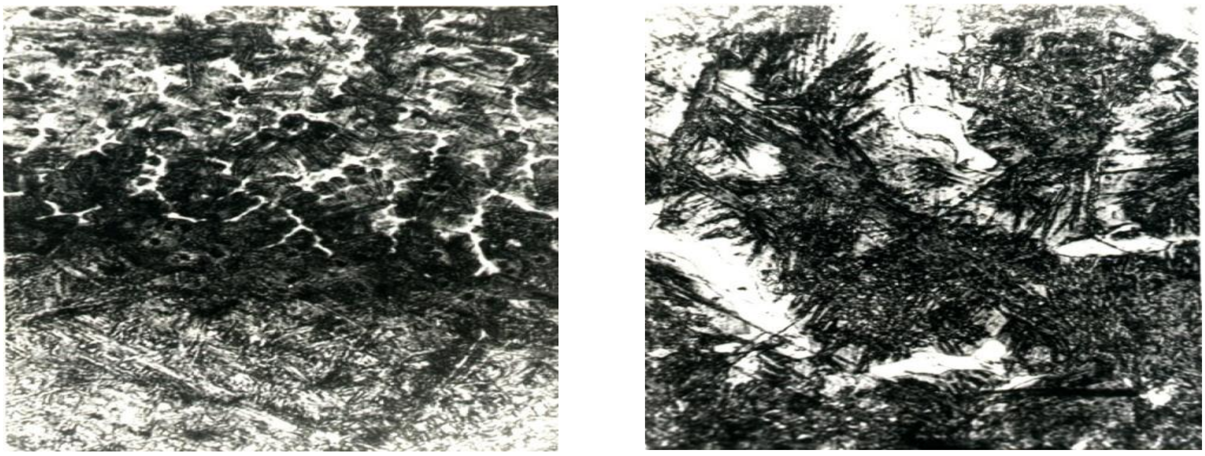
1. Introduction

To improve the mechanical properties of welded joints made on low carbon steels, various thermal and thermochemical treatments are applied. One of the commonly used thermochemical treatments is silicification [5]. It consists in enriching the surfaces of welded parts with silicon atoms, which enter into chemical combinations with the other chemical elements in the structure, forming cementite alloyed with silicon and silicon carbide [6]. This results in a hardening of the surface of the welded joints and an increase in the resistance to the wear phenomenon. The use of mechanical vibrations during the silicification process, leads to the acceleration of chemical reactions and the deeper penetration of silicon into the metal subjected to silicification [9].

In the first stage, it was made a study on the thermodynamics of the silicification process. It was analyzed the possibility of obtaining chemical reactions during the silicification process. These chemical reactions may involve several substances that react with each other to produce protective compounds. The possible chemical reactions depend very much on the value of the variation of the free enthalpy. In this way it can be estimated whether the chemical reaction is possible or not [7]. The researches show that if we use vibrations during thermochemical treatments, the deposited silicate layer increases. Therefore, the energy introduced by vibration contributes to the development of the silicate layer. The energy developed by mechanical vibrations can increase the temperature, and in this way can contribute to the growth of the silicate layer. The vibrations also have an important role in attenuating internal stresses created by the thermal field. By silicification, they can be created conditions to achieve chemical reactions, that help at the protection of welded joints made on low-carbon steels [2].

The enrichment of the surface layer with silicon aims to increase the resistance of welded parts to wear. The silicification process can be performed in a gaseous, liquid or solid medium. In the presence of mechanical vibrations, the diffusion of silicon is very much stimulated.

This phenomenon is observed in the microstructures shown in Figure 1, where a very pronounced diffusion of silicon was recorded, at the grain boundary [1].



100X 350X

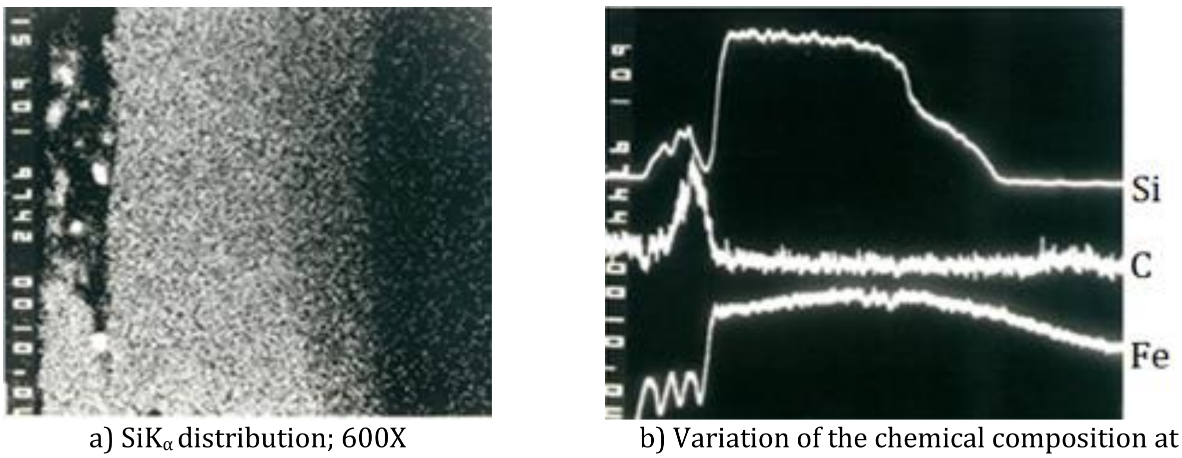
Fig. 1. Microstructure of a welded piece of CC 45 steel, silicified

The sample was silicified using high frequency currents. The very high temperature and the high heating speed are increasing the diffusion at the grain boundary, where the crystal lattice has many defects. By applying high heating speeds, the diffusion speed can increase several times. The higher the heating rate is, the finer the austenite will be and the smaller the grain size will be, when reaching certain temperatures [4].

Examining the influence of the alloying elements on the silicification process of the welded steel parts, it was noticed a very high influence of the carbon content on the diffusion mechanism of silicon. The other alloying elements studied have a much smaller influence on the diffusion of silicon in welded steel parts than carbon. As silicon is a ferritic structural element, it narrows the austenitic field at steels. The silicate layer has a ferrite structure alloyed with silicon. At higher silicon concentrations, the silicon-alloyed cementite (Fe_4CSi, Fe_6CSi, etc.) and the silicon carbide are initially formed. The rest of the carbon atoms are dislocated by the silicon atoms and they are forced to diffuse to the core of the part. For welded parts subjected to silicification, it is recommended to use low carbon steels [8].

2. Siliconization Tests of the Welded Joints Made Of Construction Steels With and Without the Use of Mechanical Vibrations

The siliconization tests were done on welded joints made of construction steels with the application of mechanical vibrations. Figure 2 shows the distribution of some elements, based on the analysis at the electronic microprobe for the welded joint made on CC 45 steel, silicified with vibrations, frequency 230 Hz and power P = 850 W [1].



a) SiK_{α} distribution; 600X b) Variation of the chemical composition at the microprobe

Fig. 2. The results of the microprobe analysis of the siliconized CC 45 steel with paste at 950 °C, vibrated

Figure 3 shows the distribution of the alloying elements for CC45 siliconized steel, without the use of mechanical vibrations. In both samples, the layer contains approx. 13 ... 14% Si, and their thickness is different. It is higher in the case of using vibrations at the welded part.

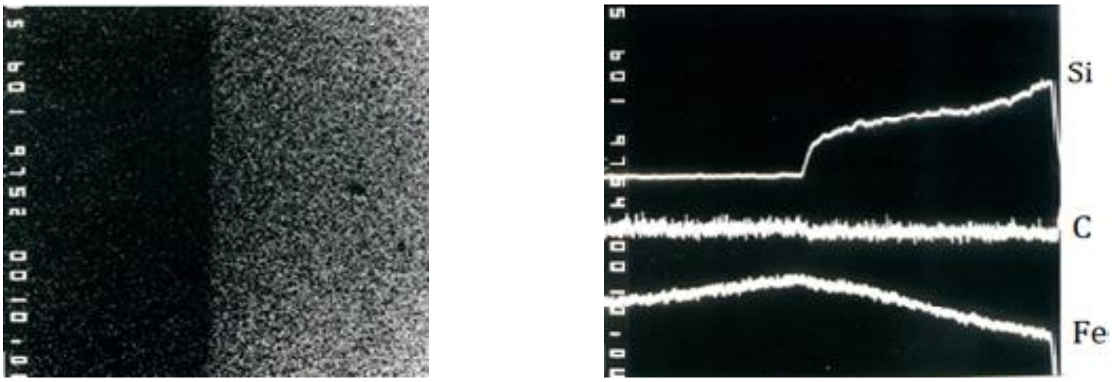


Fig. 3. The results of the microprobe analysis of the siliconized CC 45 steel with paste at 950 °C, non-vibrated (Holding time 6 hours)

In the first stage of the study of the thermodynamics of the silicification process, a small number of possible chemical reactions were studied. A number of eight chemical substances participate in these reactions. In the second stage, when developing the electronic computer program, the number of chemical substances studied, increases to 21. In this way, it becomes possible to write and verify a very large number of chemical reactions, that are possible in the silicification process of welded joints.

The thermodynamic data of the substances, studied in the first stage, are: Fe; $SiCl_4$; $FeCl_2$; Si; $FeCl_3$; $SiCl_2$; H_2; HCl. For the silicon dichloride, they were calculated the enthalpy and the entropy based on the report between the dissociation energies of tetrachloride and silicon dichloride [1]:

$$D''(SiCl_2) = \frac{3}{5}D''(SiCl_4) \quad (1)$$

$$\Delta H^0(SiCl_2) = -85.5 \text{ kcal/mol}; \quad (\Delta H^0 = \text{Enthalpy energy}) \quad (2)$$

$$S^0(SiCl_2) = 47.5 \text{ cal/mol×deg} \quad (3)$$

3. The Equations of Variation of the Free Enthalpy Regarding the Exchange Reaction between Sicl4 and Fe

In order to be able to analyze the behavior of the free enthalpy of Gibbs at a certain temperature, it is taken into consideration the chemical reaction that takes place between the chemical elements such as Fe and $SiCl_4$. It is established the value of the corresponding enthalpy ΔH^0, as well as the entropy ΔS^0, then it is calculated the Gibbs free enthalpy, ΔG^0. Z_0 is a variable depending on the temperature at which the chemical reaction takes place.

The free Gibbs enthalpy was calculated for temperatures of 1100 °K; 1300 °K and 1500 °K, and it shows the energy developed by the chemical reaction:

$$2Fe + SiCl_4 \rightarrow 2FeCl_2 + Si \quad (4)$$

$$\Delta H^0 = -21300 \text{ cal/mol} \quad (5)$$

$$\Delta S^0 = -28.9 \text{ cal/mol×deg}; \quad (\Delta S^0 = \text{Entropies}) \quad (6)$$

$$\Delta c^o_p = -25.07 \text{ cal/mol×deg} \quad (7)$$

$$\Delta G^0_T = -21300 + T×28.9 + 25.07×Z_0×T, \quad \text{in [cal/mol]} \quad (8)$$

a) T = 1100 °K $Z_0 = 0.5765$ (9)

$\Delta G^0_{1100} = +\ 26787$ cal/mol; (ΔG^0=Gibbs free enthalpy energy) (10)

b) T = 1300 °K $Z_0 = 0.7019$ (11)

$\Delta G^0_{1300} = +\ 39720$ cal/mol (12)

c) T= 1500 °K $Z_0 = 0.8141$ (13)

$\Delta G^0_{1500} = +\ 53435$ cal/mol (14)

Assuming that iron trichloride is formed as a result of the exchange reaction, we have the following chemical reaction:

$$4Fe + 3SiCl_4 \rightarrow 3Si + 4FeCl_3 \quad (15)$$

Thermodynamic calculations are very laborious, but knowing the value of the variation of the free enthalpy, it can be appreciated whether the studied chemical reaction can take place or not. The free enthalpy value also indicates the reaction speed. The use of the computer allows very fast calculations, followed by the visualization of the variation curve of the free enthalpy with the temperature [9].

For this purpose, a program was developed, which allows a quick appreciation of the reaction possibilities, based on thermodynamic calculations, such as those presented above. The program contains the thermodynamic constants of these substances, and by permuting them, a large number of chemical reactions can be tested. The program can also test chemical reactions for nitriding or carbonitriding.

After obtaining the variation of the free enthalpy, the variation of it, is represented graphically as in Figure 4 [1].

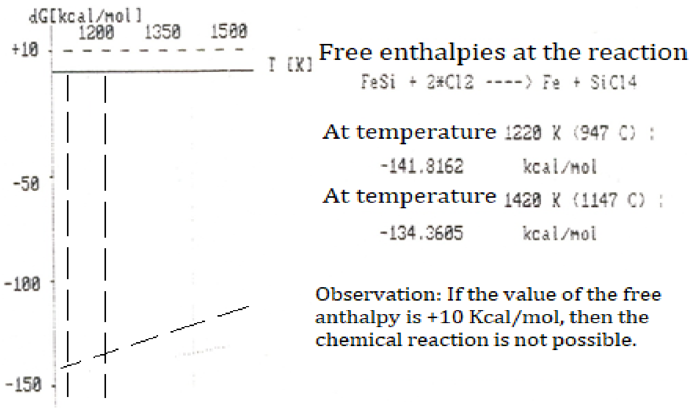


Fig. 4. Free enthalpy variation with temperature

On the graphic in Figure 4, at +10 kcal/mol, a horizontal line appears, which indicates the maximum value of the free enthalpy variation, at which the chemical reaction is thermodynamically possible. Also, the temperature range of interest for silicification is delimited by two vertically interrupted lines, at 947 °C, respectively at 1147 °C. Next to the graphic, appears the studied chemical reaction, and below are given the values of free enthalpies at 947 °C and 1147 °C. These values allow the identification of extreme situations, namely if the free enthalpy has values above +20 kcal/mol, the curve does not appear on the graph and the reaction is not possible. If the free enthalpy has values below −180 kcal/mol, the curve does not appear on the graph and the reaction will take place at high speed. For example, in the reaction shown in Figure 4, due to the high negative values of the free enthalpies, the reaction speed will be high and the increase in temperature will lead to a decrease in the speed reaction.

Conclusion

The samples were silicified with paste, using heating with high frequency currents. The very high temperature and the very high heating speed, greatly increase the diffusion at the grain boundary, where the crystal lattice has many defects. By applying high heating speeds, the diffusion speed can increase several times. It was noticed that when the welded joints are silicified, the higher the heating speed is, the austenite will have a finer granulation, which is a benefit for the mechanical properties of the welded joints. The carbon content has a great influence on the diffusion mechanism of silicon. The other alloying elements have a lower influence. That is why for the welded parts subjected to silicification it is recommended to have a low carbon content. Siliconization is a thermochemical treatment that brings many improvements to the surface quality of treated welded joints. These surfaces are given good mechanical properties and high corrosion resistance. The wear resistance of the silicate layers is better and the appearance of the surfaces is more uniform and lustrous.

The depth of the silicate layer depends very much on the carbon content, as well as on the other alloying elements of the silicate welded joint. Also, the depth of the silicate layer of the welded joint also depends on the processing of the base metal surface. The porosity of silicate welded joints has a great influence on the thickness of the silicate layer.

Although it is a surface coating process, silicification can also have a great influence on the mechanical properties of the base metal subjected to silicification.

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