

# **OXIDISING-DEOXIDIZING POTENTIAL OF THE CONTROLLED ATMOSPHERES FOR WELDING AND HEAT TREATMENT OF STEELS WITH THE SPECIAL SYSTEMS OF ALLOYING**

S. Shanchurov<sup>1</sup>, E. Ivanajskij<sup>2</sup>, A. Ishkov<sup>3</sup>, V. Ivanajskij<sup>3</sup>

<sup>1</sup>Regional Center of Laser Technologies, Ekaterinburg, Russia

<sup>2</sup>Altay State Technical University, Barnaul, Russia

<sup>3</sup>Altay State Agrarian University, Barnaul, Russia

## **Absrtact**

The main types of the atmospheres interacting with the heated metals and alloys are considered. The main chemical reactions proceeding in the oxidizing and deoxidizing atmospheres are shown, and their thermodynamic justification is also given. It is established that at temperatures more than 1500°K reactions of deoxidizing of metals by monoxide of carbon prevail over oxidation reactions by the oxygen which is formed at dissociation of carbon dioxide. It is shown that there are conditions under which there is no oxidation of metal in the atmosphere to the increased content of monoxide of carbon and hydrogen. It is established that as the protective atmosphere at heat treatment of steels by currents of high frequency it is possible to use the reducing flame having a quantity of oxygen, hydrogen and methane.

## **Introduction**

Processes of high-temperature heat treatment, chemical heat treatment, welding and many others proceed in specially created atmospheres. Inert Ar and He gases provide the best protection of a surface of the processed details, however the high price of these gases strongly limits the field of their application. The atmospheres on the basis of nitrogen which part about 5% of monoxide of carbon and hydrogen [1], and even up to 20% CO<sub>2</sub> and 50% of H<sub>2</sub>, in case of use of endogas [2] are much more often used. The specified atmospheres have deoxidizing properties in relation to oxides of the processed metals.

Entry in composition of protective gases of oxygen, vapors of water, carbon dioxide leads to behavior the oxidizing reactions at high temperatures. Hydrogen, carbon monoxide, saturated and unsaturated hydrocarbons on the contrary, cause deoxidizing of oxides to pure metals therefore their input to the furnace at heat treatment prevents with oxidation of a surface.

In furnaces for soldering by solid solder use the deoxidizing atmosphere of hydrogen for the purpose of elimination of surface oxides. At arc welding on the contrary, the broadest application is found by the oxidizing atmosphere containing CO<sub>2</sub> carbon dioxide, dissociating at high temperatures with formation of monoxide of CO carbon and free oxygen [3].

The negative impact of oxygen is compensated or special alloying of metal, or use of the additional liquid slags providing protection of metal against oxidation.

The technology of gas welding of steels and non-ferrous metals at which heat is generated in the process of combustion of hydrocarbons in an oxygen stream is widespread. At the same time the gas flame is considered "neutral" as it has neither oxidizing, nor deoxidizing properties. In work [4] it is offered to use the deoxidizing atmosphere of carbon monoxide when welding in the environment of protective gases.

Now in the industry more and more broad using is found for steel which structure and properties are provided with introduction of the tenth and even the 100-th shares of percent of the alloying additives. So, for example, vanadium is entered into structural steels in number from 0.08 to 0.12%, niobium from 0.03 to 0.06% [5], borium from 0.003% [6] to 0.2% [7].

Application for protection of an arc of carbon dioxide or mixes of gases on its basis can't provide the required chemical composition of weldment, in connection with what there is a need to investigate a possibility of use of products of incomplete combustion of a gas flame for protection of metal of a welding pool against oxidation.

### Methods and techniques of the conducted research

With use of the data given on the website <http://www.sciencebysimulation.com> counted the sign and size of criterion Le Chatelie ( $\Delta H^{\circ}p$ ) and isobaric and isothermal potential  $\Delta G^{\circ}p$  (Gibbs's criterion) values of entropy, an enthalpy and Gibbs's energy as a first approximation when  $C^{\circ}p$  and  $\Delta H^{\circ} = \text{const}$  [8] were defined. Calculation of theoretical sizes  $\Delta H^{\circ}p$  and  $\Delta G^{\circ}p$  under standard conditions ( $T = 298.15 \text{ K}$ ; normal atmospheric pressure) and the chosen temperatures order on the known formulas [9]:

$$\Delta H_p^{\circ}(298) = \sum v_i \Delta H_{f_{298}}^{\circ}(i) - \sum v_j \Delta H_{f_{298}}^{\circ}(j); \quad (1)$$

$$\Delta S_p^{\circ}(298) = \sum v_i S_i^{\circ}(298) - \sum v_j S_j^{\circ}(298); \quad (2)$$

$$\Delta C_p^{\circ} = \sum v_i C_p^{\circ}(i) - \sum v_j C_p^{\circ}(j); \quad (3)$$

$$\Delta H_p^{\circ}(T) = \Delta H_p^{\circ}(298) + \Delta C_p^{\circ}(T - 298); \quad (4)$$

$$\Delta S_p^{\circ}(T) = \int_{298}^T \frac{\Delta C_p^{\circ}}{T} dT = \Delta C_p^{\circ} \ln \frac{T}{298}; \quad (5)$$

$$\Delta G_p^{\circ}(T) = \Delta H_p^{\circ}(T) - T \Delta S_p^{\circ}(T); \quad (6)$$

where  $v_i$  and  $v_j$  — stoichiometric coefficients of products of reaction and initial substances respectively;  $\Delta H_{f_{298}}^{\circ}(i)$  — heat of formation of products of reaction at 298 °K;  $\Delta H_{f_{298}}^{\circ}(j)$  — heat of formation of initial substances at 298 °K;  $C_i^{\circ}(298)$  — thermal capacity of the formed reaction products at 298 °K;  $C_j^{\circ}(298)$  — thermal capacity of initial substances of reaction at 298 °K;  $S_i^{\circ}(298)$  — entropy of the formed reaction

products at 298 °K;  $S_j^0(298)$ — entropy of initial substances of reaction at 298 °K; T — reaction course temperature;  $\Delta G_p^0(T)$ — Gibbs's energy at a T temperature.

## Results and their discussion

The gas flame consists of a core, a central zone and a torch [10]. In a core there is a disintegration of molecules of hydrocarbons, and also incomplete combustion of carbon. During of combustion of hydrocarbons there is a quantity of free carbon which heated particles give a bright luminescence of a flame.

The central zone contains products of incomplete combustion and has the most high temperature and the restoring ability [11]. In this zone welding processes proceed. Depending on amount of oxygen as a part of gas mixture distinguish:

- a "normal" flame which is neutral in relation to metal and its lowest oxide. The oxygen which is available in a flame completely is spent for reburning of products of combustion. The structure of a neutral gas flame is brought in table 1;
- the "oxidizing" flame having the increased content of oxygen which oxidizes metal;
- the "carbonizing" flame in which there is an excess of combustible gas, owing to what a part of carbon doesn't burn down, and diffuses in surface layers of metal.

**Table 1.** Chemical composition of a normal gas flame

Parts of a flame	Contents on the volume, %					
	CO	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> O	N <sub>2</sub>	O <sub>2</sub>
Near the end of a core	60	31	-	-	8	-
At the end of a deoxidizing zone	33	15	9	6	33	-
In a middle part of a torch	3,7	2,5	22	2,6	58	8
Near the end of a torch	-	-	8	2,2	74	15

In a torch by means of oxygen of air there is a after flaming at the lowering temperature.

The conducted researches have shown [12] that actually welding neutral flame actively counteracts oxidation, and in certain cases deoxidizes metal of a welding pool thanks to presence of monoxide of carbon and hydrogen.

At high temperature there is a dissociation of carbon dioxide to release of atom of oxygen which forms further metal oxides. Along with oxidation processes of decarbonization of a surface proceed. Process of decarbonization of steel happens at preliminary dissociation of carbide of iron





Iron oxidation reaction proceeds at entry in the atmosphere of water vapor:



All reactions given above are reversible, at the same time, in the specified range of temperatures metal oxidation reactions spontaneously will proceed. However, follows from the data provided in work [13] that changing the maintenance of CO and H<sub>2</sub> in the protective atmosphere it is possible to achieve course of both oxidizing, and deoxidizing reactions. The deoxidizing ability of the protective atmosphere increases if with increase in temperature the maintenance of a share of hydrogen and monoxide of carbon in gas mix increases.

We will consider the possibility of interaction of oxides of the alloying elements with carbon monoxide:



In the studied interval of temperatures, reaction at which monoxide of carbon takes away oxygen from oxides, for example at iron oxide is energetically favorable, being deoxidized to carbon dioxide. This reaction is in detail investigated and is applied in metallurgy, however, spongy iron of poor quality therefore the purpose of increase in content of monoxide of carbon in the protective atmosphere is not deoxidizing of oxides to metals, and prevention of course of oxidizing reactions as a result is formed. Chrome oxides, forming superficial films, interfere with further oxidation of metal. It should be noted that silicon oxide restoration in the environment of monoxide of carbon is probable only at low temperatures.

The research of behavior of the microalloying elements when heating steel to melting temperature is of considerable practical interest above in the deoxidizing environment of the "normal" and "carbonizing" flame.



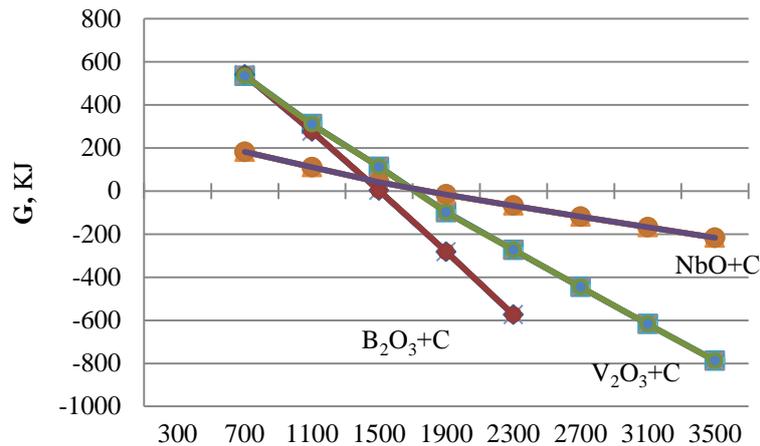
Gibbs's energy, at a temperature of 1500 °K, makes 386 KJ for reaction (16), 133 KJ for reaction (17) and 275 KJ for reaction (18). Comparable values turn out when calculating interaction of the specified oxides with hydrogen.

As it has been noted above, at a gas flame there are heated carbon particles which adjoining to heated steel, can enter chemical reactions. Interaction of oxides of

vanadium, niobium and borium with carbon dissolved in an austenite lattice is also possible.



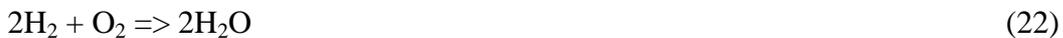
Results of calculations of change of energy of Gibbs at restoration of oxides of vanadium, niobium and borium atomic carbon are given in the Fig.1.



**Figure 1.** Change of energy of Gibbs at deoxidizing of oxides of vanadium, niobium and borium atomic carbon

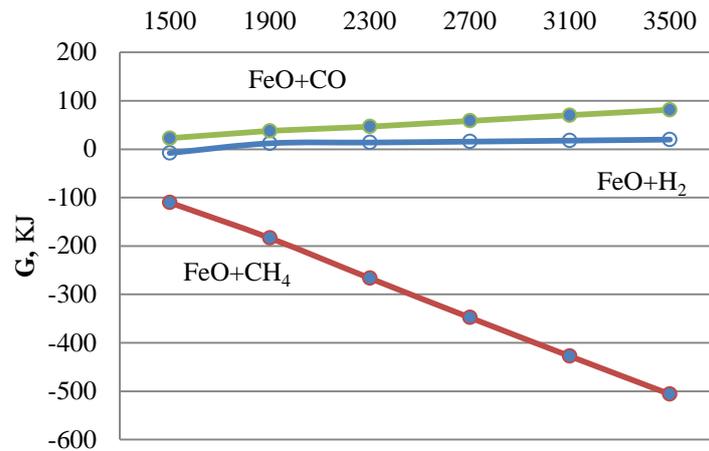
When using a "normal" flame for protection of the processed metal oxidation of microadditives is improbable as formation of oxides will be interfered by active reactions of deoxidizing.

As a part of the offered protective atmosphere there will be a quantity of oxygen which will enter oxidizing reactions with iron, hydrogen and carbon monoxide:



Gibbs's energy of the given reactions has approximately identical values, at the same time reaction (21) will proceed more vigorously that can lead to formation of a quantity of FeO. However, formation of oxidic films on the surface of metal will be interfered by presence of CO, H<sub>2</sub> and CH<sub>4</sub> at the atmosphere:





**Figure 2.** Change of energy of Gibbs at interaction of oxides of metals

Follows from the Fig. 2 that with temperature increase of the protective atmosphere the tendency to oxidation of a surface of metal will decrease.

The greatest contribution deoxidizing of activity of the protective atmosphere at high temperatures is made by  $\text{CH}_4$  which breaks up to components that considerably increases deoxidizing ability of gas mix.

The possibility of formation of nitrides on a surface of steel details, under the influence of the studied atmospheres was investigated. It is established that in the range of temperatures from 1000 °K to 1812 °K of formation of oxides and nitrides thermodynamic it is possible. The value of energy of Gibbs evenly hollow increases while the equilibrium constant increases exponential. In this regard, the kinetic factor begins to prevail and slow down formation of oxides and nitrides, even in spite of the fact that reactions still thermodynamic are allowed. Also to increase in temperature there is a shift of balance towards initial substances, that is, the probability of formation of oxides and nitrides decreases.

Formation of oxides and nitrides stops at  $T > 3842 \text{ K}$  while kinetic because the equilibrium constant grows exponential and advances growth of energy of Gibbs, full formation of oxides in this protective atmosphere stops at a  $T$  temperature  $> 1457 \text{ K}$ . For complete cessation of formation of carbon oxide the recommended pressure of the protective atmosphere is from 2 to 2.6 atmospheres on all specified intervals of temperatures.

Thus, the carried-out calculations show that introduction to composition of gases of deoxidizers like CO or  $\text{CH}_4$  allows to prevent oxidation of a surface of the heated samples in case of heating of gases.

By results of calculations the gas atmospheres containing up to 10% of  $\text{CH}_4$  have been prepared. These atmospheres were used for protection of the details heated by currents of high frequency when carrying out process of quenching. Because temperature of heating of metal exceeded flash temperature, there was an ignition given from gases, to formation of the nontoxic  $\text{CO}_2$  and  $\text{H}_2\text{O}$  components.

Samples after heat treatment had no formation of oxide films on a surface.

## Conclusions

1. When heating details in the atmosphere which is mainly consisting of monoxide of carbon and methane there are no iron oxidation reactions.
2. Existence in the atmosphere of strong deoxidizers (CO, H<sub>2</sub>), when heating steel to melting temperature and above, doesn't lead to oxidation of a surface of a product, even in case of presence at the gas of a quantity of oxygen that allows to carry out protection of a product a deoxidizing gas flame.
3. This conclusion extends to other metals, for example copper, the having smaller affinity to oxygen, than iron.
4. At interaction of the offered protective atmosphere to oxygen of air there is its combustion, to formation of the nontoxic substances CO<sub>2</sub> and H<sub>2</sub>O.

## References

1. Nemenyi R: Controlled Atmospheres for Heat Treatment pergamon press. Southampton, The Camelot Press Ltd, 1984.
2. Sedov Yu: Reference book by the young heat-treater. Moscow, Vysshaya shkola, 1986.
3. Volchenko V: Theory of welding processes. Moscow, The higher school, 1988.
4. Ivanaysky E: A method of welding in the environment of protective gases, Control and Diagnostic Center Limited liability company, Pat No 2014100493/02 October 2015.
5. Lednikov E, Cheprasov D, Connick D: Cold resistance of welds of steel bridge structures from a high-quality mill products of steel 10CrSiNiCuA and 15 CrSiNiCuA. Polzunovsky the almanac 2017 1 84-90.
6. Parusov V: New application of borium in metallurgy. The Bulletin of MSTU of G.I. Nosov 2005 1 15-17.
7. Derkach A: Influence of borium on a microstructure and property of pipes from low-carbon austenitic chromonickel steel. Questions of atomic science and technology. "Physics of Radiation Damages and Radiation Materials Science" series 2005 5 80-86.
8. Barry T: Applied chemical thermodynamics: models and calculations. Moscow, World, 1988.
9. Ishkov A: Thermodynamic justification of chemical reactions in the B<sub>4</sub>C system – borium fluxl-Fe at HFC-heating. News of the Altai state university 2014 3 (83) 199-203.
10. Asinovskaya G: Gas welding and cladding of non-ferrous metals and alloys. Moscow, Mechanical engineering, 1974.
11. Ninburg A: Gas-flame processing of metals with use of gases, substitutes of acetylene. Moscow, Mechanical engineering, 1976.
12. Polevoi G: Gas-flame processing of metals. Moscow, Academy, 2005.
13. Bord N: Thermodynamic calculations in practice of designing and use of welding materials, Minsk, Belarusian science, 2006.