Calculation of surface tension and its temperature dependence for liquid Cu-20Ni-20Mn alloy

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Abstract
Temperature dependence of surface tension of manganese cupronickel Cu-20Ni-20Mn is defined for triplex system Cu-Ni-Mn with the use of Butler model and thermodynamic functions of liquid phase calculated according to CALPHAD methodology. For calculation of temperature dependence of surface tension of specified alloy there suggested the equation $\gamma(T)_{Cu60Ni20Mn20} = 1384,5 - 0,1735(T - 1323)$, which describes the results of experimental research to high precision.
Key words: SURFACE TENSION, BUTLER EQUATION, MANGANESE CUPRONICKEL, COMPUTING THERMODYNAMICS, CERMETS

1. Introduction

Dispersive hardening alloys of the system Cu-Ni-Mn are widely used as matrix alloys [1] in the hardwearing composite materials and coatings on the base of high-melting compounds or hard alloys, which are obtained mostly in the presence of liquid phase according to the technologies of furnace welding (for coatings) or during preservation of presintered porous ceramic frames (for products). When choosing technological parameters of such processes, one of the necessary conditions is the estimation of surface tension of binding alloy in the wide range of temperatures, which defines the growth kinetics of soaked layer depth. This in its turn allows to avoid excessive isothermal holding, when uncontrolled diffusion processes, leading to the reduction of the level of mechanical properties, are being developed. Literary data on surface tension of alloys of Cu-Ni-Mn system are limited, for example, in work [2] the results of experimental studies on measurement of a surface tension of an alloy of MNMTs 60-20-20 (Cu-20Ni-20Mn) by method of a maximum pressure in a gas bubble only in the range of temperatures of 1260 - 1280°C are presented. As the temperature range of receiving the products and coatings with use of an alloy of Cu-20Ni-20Mn is much wider [3], there is a need of an assessment of its surface tension within the temperatures of 1050 - 1400°C. From there, **the aim of the work** is the development of analytical model for calculation of a surface tension of manganese cupronickel Cu-20Ni-20Mn alloy with the use of Butler equation [4] and thermodynamic functions of liquid phase in Cu-Ni-Mn system [5] within the CALPHAD method [6].

2. Calculation model

According to Butler's equation the surface tension (γ) for multicomponent fusion is the function of physical properties of components and thermodynamic parameters of their interaction. Thus the surface monoatomic layer is considered as the independent phase, which is in balance with other volume of fusion. For the system consisting of n components the equation for a surface tension (γ_n) can be written as follows:

$$\gamma_n(T) = \gamma_i + \frac{RT}{A_i}\ln\left(\frac{c_i^S}{c_i^B}\right) + \frac{1}{A_i}\left\{{}^E G_i^S\left(T, c_i^S\right) - {}^E G_i^B\left(T, c_i^B\right)\right\}, (i = 1,2...n) \quad (1)$$

where γ_i – is a surface tension of the i^{th} component, J/ m^2; R – is a multiple-purpose gas constant, J/mol · K; A_i – is a surface area of a monoatomic layer of a liquid component, m^2; c_i^C and c_i^B – are the surface and volume concentration of components, respectively, at. fraction; ${}^E G_i^S$ and ${}^E G_i^B$ – are superficial and volume partial pressure free energy of a component, respectively, J/mol.

The value A_i according to [7] is calculated as follows:

$$A_i = 1,091 N^{\frac{1}{3}} V_i^{\frac{2}{3}} \quad (2)$$

where N – Avogadro constant; V_i – molar volume of pure component, cubic meters.

The value ${}^E G_i^B$ is determined with the help of excess energy of the system (${}^E G^B$) according to the equation:

$${}^E G_i^B\left(T, c_i^B\right) = {}^E G^B + \left(1 - c_i^B\right)\frac{\partial {}^E G^B}{\partial c_i} \quad (3)$$

in its turn excess energy of system in the form of Redlikha-Kister's polynoms [8] is determined by a formula:

$${}^E G^B = \sum_{i=1}^{2}\sum_{j>1}^{3} c_i^B c_j^B \sum_{v=0}^{1} {}^v L_{ij}(T)\left(c_i - c_j\right)^v \quad (4)$$

where L_{ij} – are the interaction parameters.

At the known value of ${}^E G_i^B$, value ${}^E G_i^S$ is suggested to be determined by a formula[9]:

$${}^E G^S \approx 0,83\,{}^E G^B \quad (5)$$

3. Results and their discussion

For the threefold *Cu-Ni-Mn* system the equation (1) looks as follows:

$$\gamma_{CuNiMn}(T)=\gamma_{Cu}+\frac{RT}{A_{Cu}}\ln\left(\frac{1-c_{Ni}^{S}-c_{Mn}^{S}}{1-c_{Ni}^{B}-c_{Mn}^{B}}\right)+\frac{1}{A_{Cu}}\left\{{}^{E}G_{Cu}^{S}\left(T,c_{Ni}^{S},c_{Mn}^{S}\right)-{}^{E}G_{Cu}^{B}\left(T,c_{Ni}^{B},c_{Mn}^{B}\right)\right\}$$

$$=\gamma_{Ni}+\frac{RT}{A_{Ni}}\ln\left(\frac{c_{Ni}^{S}}{c_{Ni}^{B}}\right)+\frac{1}{A_{Ni}}\left\{{}^{E}G_{Ni}^{S}\left(T,c_{Ni}^{S},c_{Mn}^{S}\right)-{}^{E}G_{Ni}^{B}\left(T,c_{Ni}^{B},c_{Mn}^{B}\right)\right\}$$

$$=\gamma_{Mn}+\frac{RT}{A_{Mn}}\ln\left(\frac{c_{Mn}^{S}}{c_{Mn}^{B}}\right)+\frac{1}{A_{Mn}}\left\{{}^{E}G_{Mn}^{S}\left(T,c_{Ni}^{S},c_{Mn}^{S}\right)-{}^{E}G_{Mn}^{B}\left(T,c_{Ni}^{B},c_{Mn}^{B}\right)\right\} \quad (6)$$

Temperature dependences of a surface tension for pure Cu, Ni and Mn according to work [10] are мJ/ m^2:

$$\gamma_{Cu}=1355-0{,}19(T-1358);$$
$$\gamma_{Ni}=1796-0{,}35(T-1728);$$
$$\gamma_{Mn}=1100-0{,}35(T-1519). \quad (7)$$

Partial pressure of Gibbs's energy of components in fusion may be presented according to [9] in the form:

$${}^{E}G_{Cu}^{B}\left(T,c_{Mn}^{B},c_{Ni}^{B}\right)={}^{E}G^{B}-c_{Mn}^{B}\frac{\partial\,{}^{E}G^{B}}{\partial c_{Mn}}-c_{Ni}^{B}\frac{\partial\,{}^{E}G^{B}}{\partial c_{Ni}}$$

$${}^{E}G_{Mn}^{B}\left(T,c_{Mn}^{B},c_{Ni}^{B}\right)={}^{E}G^{B}+\left(1-c_{Mn}^{B}\right)\frac{\partial\,{}^{E}G^{B}}{\partial c_{Mn}}-c_{Ni}^{B}\frac{\partial\,{}^{E}G^{B}}{\partial c_{Ni}}$$

$${}^{E}G_{Ni}^{B}\left(T,c_{Mn}^{B},c_{Ni}^{B}\right)={}^{E}G^{B}-c_{Mn}^{B}\frac{\partial\,{}^{E}G^{B}}{\partial c_{Mn}}+\left(1-c_{Ni}^{B}\right)\frac{\partial\,{}^{E}G^{B}}{\partial c_{Ni}} \quad (8)$$

where ${}^{E}G^{B}$ for the system *Cu-Ni-Mn* after substitution looks as follows:

$${}^{E}G^{B}=c_{Cu}^{B}c_{Ni}^{B}L_{Cu:Ni}+c_{Cu}^{B}c_{Mn}^{B}L_{Cu:Mn}+c_{Mn}^{B}c_{Ni}^{B}L_{Mn:Ni}+c_{Cu}^{B}c_{Ni}^{B}c_{Mn}^{B}L_{Cu:Ni:Mn} \quad (9)$$

Temperature dependences of parameters of interaction (L) according to work [5] look as follows:

$$L_{Cu:Ni}=(11760+1{,}084T)+(-1672)(c_{Cu}^{B}-c_{Ni}^{B});$$
$$L_{Cu:Mn}=(1800-2{,}28T)+(-6500-2{,}91T)(c_{Cu}^{B}-c_{Mn}^{B});$$
$$L_{Ni:Mn}=(-85853+22{,}715T)+(-1620+4{,}902T)(c_{Ni}^{B}-c_{Mn}^{B});$$
$$L_{Cu:Ni:Mn}=(-7000)c_{Cu}^{B}+(25000-50T)c_{Ni}^{B}+(-111000+50T)c_{Mn}^{B}. \quad (10)$$

Surface areas of monoatomic layers of components after substitution of values in the equation (2) will be:

$$A_{Cu}=1{,}091(6\cdot10^{23})^{\frac{1}{3}}(7{,}1\cdot10^{-6})^{\frac{2}{3}};\ A_{Ni}=1{,}091(6\cdot10^{23})^{\frac{1}{3}}(6{,}5\cdot10^{-6})^{\frac{2}{3}};\ A_{Mn}=1{,}091(6\cdot10^{23})^{\frac{1}{3}}(7{,}1\cdot10^{-6})^{\frac{2}{3}}. \quad (11)$$

For manganese cupronickel the composition in atomic fraction was accepted as: c_{Cu}^{B}=0,57259; c_{Ni}^{B}=0,20664; c_{Mn}^{B}=0,22077. Thus, after substitution of values of the equation (7-11) into the equation (6) the system of the equations with two unknown values c_{Ni}^{S} and c_{Mn}^{S} was obtained. Temperature dependence of surface tension was defined under set temperature T with the help of this system. The values thus obtained were compared with experimental data of work [2]. Results (fig. 1) show that calculation data with high precision describe the results of experiment (deviation does not exceed 1%). Thus temperature depen-

dence of surface tension of an alloy of Cu-20Ni-20Mn is described with the value of corrected determination coefficient, which is equal to 0.99987 by the equation, mJ/m²:

$$\gamma(T)_{Cu60Ni20Mn20} = 1384,5 - 0,1735(T - 1323) \quad (12)$$

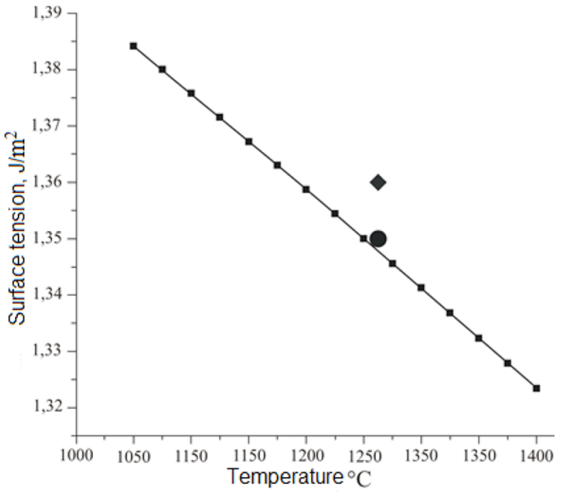

Figure 1. Temperature dependence of surface tension of manganese cupronickel Cu-20Ni-20Mn: ■ – calculation; ● – the values obtained at immersion of restrictor on 4, 10 and 16 mm² [2]; ♦ – average result according to [2]

It should be also marked that according to results of calculation, distribution of elements in the volume and on surface significantly differs especially according to the content of manganese (fig. 2), which concentration in surface layer is nearly 1.4 times higher. Considering that manganese proves as interphase-active element to a number of refractory joints in ceramics metal system [11] increase of its concentration on the surface leads to the reduction of contact angle in the specified systems, that in its turn creates favorable conditions for receiving of cermet by methods of liquid-phase sintering and preservation.

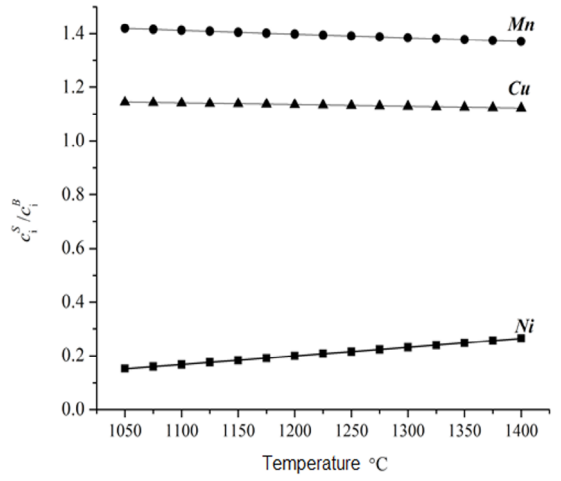

Figure 2. Temperature dependence of a ratio of components of an alloy of Cu-20Ni-20Mn on a surface and in volume of fusion

4. Conclusions

It is shown that the use of the equation of Butler for fusions of Cu-Ni-Mn system allows to calculate with high precision the value of a surface tension of an alloy of the MNMTs 60-20-20 grade within the temperature range 1050 – 1400 ºC. At temperature increase there observed the reduction of surface tension of the specified alloy on linear dependence. Thus the major part of *Mn* is concentrated in surface coating (which is also typical for manganese steels [12]). It creates prerequisites for wettability improvement by manganese cupronickel of ceramic materials and whereby it promotes obtaining of cermet in the system: ceramics – Cu-20Ni-20Mn.

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Forming Process of Automotive Body Panel based on Incremental Forming Technology

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Abstract
Development of new vehicle model is a long-time and high-cost procedure traditionally. In this paper, the typical automotive body panel has been formed by means of Single Point Incremental Forming (SPIF) technology which is high-flexibility, short-cycle, low-cost and so on. Based on the stereolithography (STL) triangle meshes, the SPIF main direction of the automotive body panel has been determined. In accordance with the partial fracture on the panel concave surface, the forming principles on single-stage and double-stage have been analysized. Multi-stage forming has been applied to realize the automotive panel processing successfully. To ensure the SPIF efficiency and quality, the first-stage forming process has been to finish the preliminary integral forming for the parts according to the concave intermediate shape, and then to conduct the second-stage forming for the concave final shape locally. The experimental data has showed that the reasonable forming stage can effectively optimize the thickness distribution of the parts. It is helpful to new vehicle development based on the SPIF flexible manufacturing technology in the future.
Key words: AUTOMOTIVE BODY PANEL, SINGLE POINT INCREMENTAL FORMING, MULTI-STAGE FORMING, THICKNESS DISTRIBUTION