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CALCULATED EVAUATION OF APPLICATION OF NANOSIZED PARTICLES IN MODIFYING THE CAST STRUCTURE OF WELD METAL

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The work deals with the features of application of promising nanosized particles of TiC, WC, TiB_2 for modifying the weld microstructure in aluminium alloy welding. Evaluation of their applicability was performed from the viewpoint of thermodynamic stability in the melts of commercial weldable alloys, which contain: Cu, Fe, Zn, Mn, and Ti. It is shown that despite their relative instability, nanosized TiC particles can be used with success as modifiers of aluminium alloys of Al–Mg system. Here, presence of silicon lowers titanium carbide resistance in aluminium melt and, therefore, is undesirable, whereas titanium, contrarily, improves the stability of TiC particles. WC particles can be used with success for modifying the structure of alloys of Al–Si system, presence of silicon increasing their stability in the melt. Particles of titanium diboride TiB_2 are the most stable compound of the studied ones. Its small modifying effect on aluminium alloys is compensated by its stability in aluminium melts at overheating. 16 Ref., 1 Table, 5 Figures.

Keywords: automatic welding of aluminium, nanosized particles, modifying, thermodynamics, filler materials

Tendencies in development of modern mechanical, automotive engineering and shipbuilding point to a steady growth of the demand for light-alloy structural elements, in order to reduce the weight of components and mechanisms, as well as fuel consumption, that is particularly important in the period of transport transition from hydrocarbon to electric engines. In a modern car with internal combustion engine the weight of aluminium alloy elements relative to overall car weight increases every year. In batch-produced cars with an electric motor this value already is on the level of 50-85 %. Here, welding remains to be the main method of joining aluminium alloy parts in automotive and aviation engineering. A high demand for aluminium structures motivated materials scientists to create new light-alloy materials based on aluminium, as well as composite materials. Appearance of new aluminium alloys and materials on their base, sharply raises the question of ensuring their reliable joining in the structure. Here, the classical weldable filler alloys based on Al-Mg and Al-Si alloying systems, do not provide the required level of mechanical properties of the weld metal relative to modern alloy characteristics, to say nothing of the composite materials. Alongside application of advanced high-strength aluminium alloys, the number of composite materials consisting of aluminium alloy matrix and filler, namely particles, fibres, whiskers, etc, is growing. Such an approach allows an essential increase of service properties of the welded joint, compared to monometallic weld. Welding of the new high-strength aluminium alloys, as well as aluminium matrix composites on their base, today has some difficulties, which require a solution. The main problem of welding new multicomponent aluminium alloys is an insufficient level of the properties of the weld, formed using commercial welding wires, as well as alloying element loss during welding, both from the part body and from the filler material. On the other hand, the welded joint of composite materials, using standard aluminium welding wires a priori has the mechanical property level, lower than that of the composite materials, manufactured on the base of aluminium alloys, strengthened by a composite component.

The structure of metal of the weld of aluminium and its alloys depends on many parameters, and if we ignore the structural features of welding equipment, the other can be conditionally divided into two groups: first group of parameters is determined by physico-chemical properties and phenomena, associated with base and filler materials; the other group includes the temperature-time mode of the welding process, impact of fluxing and modifying additives, rate of pool cooling and other parameters, which di-

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rectly affect the solidification parameters. Modifiers of the second kind have a significant impact on the solidification parameters, and on the weld macro- and microstructure, accordingly. Their impact is related to contact effect on the process of crystallization center nucleation. At addition to the melt of a modifier which has or forms bonds with a structure isomorphous to the alloy crystallites, an essential reduction of the range of melt metastability occurs, and, hence, microstructure refinement. The content of this type of modifier usually does not exceed 0.1 wt.% [1].

The work is devoted to the problem of modifying the weld microstructure by nonmetallic nanosized particles, namely to investigation of resistance of carbides and borides in aluminium melts, which act as microstructure modifiers, when added to the composition of weldable filler material for aluminium alloy welding.

At modification of aluminium and its alloys, titanium, zirconium, scandium, etc. can be regarded as classical metal modifiers of aluminium alloys. In welding, burning out or leveling of their action always occurs, due to interaction with interstitial elements and flux components. An optimum modifier is a chemically resistant, superfine (nanosized) particle, that maximally meets the requirements of crystalline compliance, that is it effectively refines the grain at minimum concentration, stays in an inert (stable) dispersed condition in the melt; has minimum structural difference from the filler alloy crystalline lattice; does not lose its modifying properties at remelting. One of the obvious solutions is adding to the weld metal of the welded joint the submicro- and nanosized nonmetallic hardeners (modifiers in the form of refractory particles, for instance carbides, oxides, borides, etc.), which, on the one hand, can modify the weld structure and are «insensitive» to local overheating during welding, and on the other hand, increase the overall strength level of the material by Orowan mechanism, creating obstacles to the movement of dislocations and cracks, which initiate.

The following can be regarded as typical nonmetallic modifiers of aluminium microstructure: TiC (at lattice parameter a = 0.4328 nm), as well as TiB₂, AlB₂, in which compliance with aluminium lattice occurs only between the close packing directions, between the second close packed plane of the aluminium matrix and second close packed plane of modifier particles. There is also data on the effectiveness of application of WC particles as modifiers for aluminium alloys of Al–Si alloying system. These particles can refine the primary and eutectic silicon in the cast structure [2, 3]. At this moment, there exists a group of modifying additives, the action of which is based on interaction in Al–Ti–C system [4, 5]. In these modifiers TiC particles are used as nucleating agents. The main advantage of such modifying additives is the possibility of their application in aluminium alloys, where the alloying components (Zr, Cr, Li, etc.) block the effect of B- and Ti-based modifiers [6, 7].

Despite the fact that the modifying effect of TiC particles has been proved in practice [8], there is also data on instability and degradation of titanium carbide particles with formation of thermally unstable and hygroscopic aluminium carbide Al_4C_3 and silicon carbide SiC [9].

Thus, at application of titanium carbide, it is necessary to study the conditions of its stability as to thermal modes of its application and alloying components of aluminium alloys. A number of studies are devoted to problems of phase interaction at interaction of carbides with aluminium alloys [10-12]. Interphase interaction in these systems can occur rather actively, and it depends on many factors, namely presence of oxide film, diffusion rate, temperature modes, interface cleanliness, etc. Direct thermodynamic calculation of phase transformations yields results, which are not always confirmed experimentally, but it is rather difficult to purely experimentally study such processes, as result repeatability is relatively low. This is the cause for availability of contradictory data in publications on carbide and boride interaction in the form of superfine particles with aluminium-based melts in solid-liquid contact. As the effectiveness of modifying impact of nonmetallic compounds on the aluminium matrix will be directly proportional to the effective contact area of the surface of these particles with aluminium melts, refinement of their dimensions to nanosized values should increase their reactivity and crystal forming ability to the same extent. Thus, such nanosized particles can vigorously react in the presence of thermodynamic conditions of reaction running and its rate that in the case of «slow» solid-phase reactions can be compensated by a large area of their running owing to the developed surface. Thus, modifying effect of nanosized particles can be leveled out, because of interaction aluminium melt components, even during the short time of existence of liquid metal weld pool.

Thermodynamic evaluation of interphase interaction of the mentioned nanosized particles was performed by a procedure, described in work [13], which is based on CALPHAD thermodynamic calculation of heterogeneous systems and takes into account the equilibrium processes in systems, proceeding from thermodynamic data for binary and ternary element

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systems that participate in the calculation. This method allows optimizing the data from different sources, calculating the dependencies, which quite well agree with experimental data.

In order to calculate the Gibbs energy functions of pure elements, their stable and unstable phases were taken from SGTE data bases [14], the majority of thermodynamic functions for binary and ternary compounds were taken from CIST2 base, data for ternary compounds and optimization of Al–C–Ti system were taken from work [15].

The model of substitution solution was used to describe the liquid phases:

$$G_{\rm m}^{\rm liq} = \sum_{i} x_i^{0} G_i^{\rm liq} + RT \sum_{i} x_i \ln(x_i)_{\rm m}^{\rm liq} + {}^{E} G_i^{\rm liq},$$

where x_i is the molar fraction of the *i*-th component; ${}^{0}G_{i}^{\text{liq}}$ is the Gibbs molar energy of the pure component and in the liquid state; *R*, *T* are the universal gas constant and absolute temperature, respectively; ${}^{E}G_{m}^{\text{liq}}$ is the excess molar Gibbs energy, defined as:

$${}^{E}G_{m}^{\text{liq}} = \sum_{i} \sum_{j>1} x_{i} x_{j} L_{i,j}^{\text{liq}} + \sum_{i} \sum_{j>i} \sum_{k>j} x_{i} x_{j} L_{i,j,k}^{\text{liq}},$$

where $L_{i,j}^{\text{liq}}$ and $L_{i,j,k}^{\text{liq}}$ are the parameters of double and triple interaction, respectively, which are described by Redlich–Kister polynomial

$$L_{i,j}^{\text{liq}} = \sum_{i} (x_i - x_j)^{n} L_{i,j}^{\text{liq}}$$

Thermodynamic parameters (Gibbs energy and enthalpy) of solid phases were determined using the regular solution model [16], in which the Gibbs energy of the *i*-th phase $\Delta G_i = \Delta G_i(T)$, which consists of three components A, B, and C, where A is the solid solution base, the Gibbs energy of which is described as

$$G_{i} = \chi A G_{i} A = \chi B G_{i} B + \chi C G_{i} C = \chi A \chi B L_{i} A, B =$$

= $\chi A \chi C L_{i} A, C + \chi B \chi C L_{i} B, C + \chi A \chi B \chi C L_{i} A, B, C +$
+ $RT(\chi A \ln \chi A + \chi B \ln x B + \chi C \ln \chi C),$

where χn , n = A, B, C is the molar concentration of component *n* in the solid solution in units of one $(\chi A + \chi B + \chi C = 1)$, $G_{in} = G_{in}(T)$ is the Gibbs energy of *n*-th component of the solution (*i*-th phase); L_i is the parameter of pair (A–B, A–C, and B–C) and triple (ABC) interaction of atoms in phase *i*, which characterize the excess entropy of component mixing relative to an «ideal solution», in which $L_i = 0$.

Calculation of the initial equilibrium state in the system was performed using as initial values the thermodynamic data for the chemical elements and TiC, which were considered as the system initial elements. Thus, in order to study the multicomponent systems of aluminium alloy-superfine particle, the following boundary conditions were established:

• a closed heterogeneous system of particle-melt is considered;

• a particle is an independent component of calculation, the quantity of which is defined as a function of the solubility limit of the metal component in the aluminium melt at the set temperature (quantity of secondary phases that form as a result of interaction is determined by the equilibrium of chemical potentials and limited maximum content of reacting particles of up to 5 wt.%);

• final result of calculations is the thermodynamic phase equilibrium.

Phase calculation was performed from 500 °C (temperature below solidus temperature of commercial aluminium alloys) up to the temperature of 900 °C.

Used as filler materials in aluminium welding are aluminium alloys, which have such alloying, modifying and impurity elements as Cu, Mg, Si, Mn, Ti, and Fe in their composition.

In accordance with the performed calculation, the interaction of tungsten carbide with aluminium-based melts occurs in keeping with the Table and phase diagrams of secondary compounds (shown are the areas and quantity of secondary phases, which formed as a result of interaction of aluminium melt with tungsten carbide), Figures 1-3.

WC particles rather actively interact with aluminium, leading to formation of Al_4W intermetallics and aluminium carbide, the area of existence of which goes beyond the temperature limits of calculation towards higher temperatures. Al_4C_3 compound is a high-temperature brittle one; it readily interacts with moisture with formation of aluminium hydroxide $Al(OH)_3$ in the form of looseness. It is obvious that presence of aluminium carbide in the weld on the interphases is highly undesirable.

Results of calculation of the probable interaction of tungsten carbide particles with aluminium melts in the temperature range of 500-900 °C showed, that tungsten carbide particles can interact with aluminium melt with formation of Al₄W intermetallics and aluminium carbide in the quantity of up to 0.96 %. It is obvious that such a calculation does not take into account the kinetic component of such a reaction. However, as we noted above, at contact of nanosized particles with a developed surface, the relatively slow processes can be greatly accelerated due to a large contact area of such a material. Manganese and iron practically do not affect the interphase interaction of tungsten carbide with aluminium melts, even though they form intermetallic compounds with aluminium. Formation of an intermetallic with copper, Al₂Cu,

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System	(Al)+WC		(Al)+TiC		(Al)+TiB ₂	
Alloying element	$T_{\rm sol}$, °C	Secondary phases	$T_{\rm sol}$, °C	Secondary phases	$T_{\rm sol}$, °C	Secondary phases
	659	$Al_4C_{3}Al_4W$	659	Al ₄ C ₃ , Al ₃ Ti, N(Ti ₃ AlC ₂)	660	-
1 % Si	647	Al ₄ C ₃ ,WSi ₂ , Al ₄ W	651	TiSi, Al ₃ Ti, N(Ti ₃ AlC ₂)	602	-
5 % Si	573	SiC, WSi ₂	640	AI_4C_3 , TiSi, TiSi ₂ , N(Ti ₃ AlC ₂), AI_8SiC_7	577	_
1 % Mn	657	Al_4C_3 , Al_4W , Al_6Mn	653	$Al_4C_3, Al_6Mn, Al_3Ti, N(Ti_3AlC_2)$	659	Al ₆ Mn
5 % Cu	551	$Al_4C_{3}Al_4W, Al_2Cu$	553	Al ₄ C ₃ Al ₃ Ti, N(Ti ₃ AlC ₂)	554	-
1 % Fe	655	$Al_4C_{3}Al_4W, Al_3Fe$	653	Al ₄ C ₃ , Al ₃ Fe, Al ₃ Ti, N(Ti ₃ AlC ₂)	654	Al ₁₃ Fe ₄
1 % Ti	659	Al ₄ C ₃ , TiC, Al ₄ W	659	Al ₄ C ₃ , Al ₃ Ti, N(Ti ₃ AlC ₂)	664	Al ₃ Ti
1 % Mg	643	Al_4C_3, Al_4W	645	Al ₄ C ₃ , Al ₃ Ti, N(Ti ₃ AlC ₂)	644	-
5 % Mg	583	Al_4C_3, Al_4W	567	Al ₄ C ₃ , Al ₃ Ti, N(Ti ₃ AlC ₂)	659	-
5 % Zn	639	Al_4C_3, Al_4W	640	Al ₄ C ₃ , Al ₃ Ti, N(Ti ₃ AlC ₂)	640	_

Calculated parameters of interphase interaction in Al-modifying particle system

only slightly activates aluminium carbide formation; copper content of 5 % in the aluminium melt increases the probability of aluminium carbide content rising by 0.03 % from 0.96 up to 0.99 %.

Titanium presence in the base melt leads to appearance of titanium carbide TiC, formation of which is energetically more beneficial than that of aluminium carbide, i.e. this is a competitive process for Al_4C_3 formation, which lowers the probability of its appearance, and its quantity in this system, respectively (Figure 2). On the other hand, in such a system the rate of WC interaction should increase, as the process of TiC formation, as was shown above, is energetically more favourable.

Similar to copper, silicon in small quantities (up to 1 wt.%) only slightly affects WC interaction with aluminium; tungsten silicide WSi_2 forms, reducing the quantity of Al_4W intermetallic. At increase of its quantity to 5 wt.%, the mechanism of interaction in Al-WC-Si system changes completely (Figure 3). The place of Al_4W intermetallic is completely taken



Figure 1. Calculated phase ratio (wt.%) in Al–5 % WC system

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up by tungsten silicide WSi₂, and silicon carbide SiC forms instead of aluminium carbide Al_4C_2 . Thus, silicon in the quantity greater than 5 % completely blocks the probability of aluminium carbide formation, phase equilibrium shifts towards formation of tungsten silicide and silicon carbide. Both these compounds are highly resistant in aluminium melts. If we assume that the interaction of tungsten carbide particles with the aluminium melt is initiated by dissolution of the contact layer surface, then WSi₂ formation in the interphase zone should block further contact interaction, as the silicide on the surface of dispersed particles isolates the interphase zone from further interaction. Presence of alloying titanium has a positive impact on the stability and formation of secondary modifying phases. Among the secondary compounds, formation of tungsten carbide is possible, which can act as modifier of aluminium solid solution.

Calculation of probable interaction in the system of aluminium-particles of titanium carbide TiC, the results of which are presented in the Table, showed



Figure 2. Calculated phase ratio (wt.%) in 99Al1Ti-5 % WC system



Figure 3. Calculated phase ratio (wt.%) in 95Al5Si–5 % WC system

limited thermodynamic instability of Al-TiC system in the studied temperature range with formation of aluminium carbide, as a result of titanium carbide dissolution. It is obvious that the maximum quantity of formed aluminium carbide is proportional to maximum solubility of titanium in aluminium for the specified temperature. That is, increase of weld pool temperature can nominally lead to increase of the quantity of formed aluminium carbide, as temperature increase raises the limit of titanium solubility in aluminium. As interaction of TiC and aluminium melt proceeds through dissolution in liquid aluminium, it is obvious that if the alloy being welded is first alloyed by titanium or boron-titanium modifier, such an interaction will be blocked, and titanium carbide particles will be thermodynamically stable.

As one can see from the Table, in the main study the chemical elements only slightly alter the interaction in this system, except for silicon, the action of which highly increases the probability of matrix alloy







Figure 5. Calculated phase diagram of Al10Si0.4Mg–TIC

interaction with the filler that is, primarily related to silicon reactivity and its ability to form titanium silicides. Silicon presence in the quantity of up to 1 % practically does not affect the interaction of titanium carbide particles with the aluminium melt. At silicon concentration below 1 % in the system, N-phase with the decrease undergoes U-type transformation with aluminium melt (L + N↔ε(Al₂Ti) + TiSi), forming phases, which can act as effective modifiers of aluminium solid solution (Figure 4). Silicon interaction with titanium carbides is thermodynamically favourable already at temperatures of solid-phase interaction, where titanium silicide TiSi can actively form due to interaction with silicon. Considering that the solid-phase diffusion processes run several orders of magnitude slower than the liquid phase processes and the negligibly small solubility of silicon in aluminium solid solution, the probability of such interaction is extremely small.

At higher concentrations of silicon in the system above 5 wt.% (Figure 5), N-phase below 1200 °C goes into chemically more stable titanium silicides, which have no modifying effect. Chemical interaction of aluminium with carbon and reduction of aluminium oxide proceed through oxicarbides and carbides. Reduction results in formation of simple (SiC, Al_4C_2) and complex refractory carbides ($Al_4SiC_4 = Al_4C_3 \cdot SiC$; $Al_{s}SiC_{7} = 2Al_{4}C_{3} \cdot SiC$, which together with oxicarbides can slow down the process of further interaction of TiC particles. Depending on silicon concentration, equilibrium carbide can appear in different compositions: Al_4C_3 or in the form of Al_2OC – at a low content of silicon and presence of aluminium oxide (from the aluminium surface). At higher silicon content Al₈SiC₄ already forms. If silicon content in the system is above 30 %, SiC formation will be thermodynamically favourable. At 1740 °C, high-temperature ternary N-phase (Ti_3AlC_2) starts forming by quasibinary peritectic transformation, as a result of interaction of initial TiC particles with the melt [15].

Particles of titanium diboride turned out to be the most stable compound in this system among the studied ones (Table). It remains thermodynamically stable in the entire studied range of temperatures, and presence of alloying elements typical for weldable aluminium alloys practically does not affect the system, and it remains inert to aluminium melts at the specified temperatures.

Conclusions

Thus, thermodynamic calculations were used to analyze the probability and establish the parameters of contact interaction of nanosized particles (WC, TiC, TIB₂) with filler material melts for weldable aluminium alloys. Established regularities of interphase interaction in the considered systems of aluminium alloy–dispersed particles, allow formulating the recommendations on selection of combinations of aluminium matrix alloy and strengthening modifying additive in the form of refractory particles, taking into account their probable interaction and modifying effect on weld metal microstructure.

It was established that finely-dispersed particles of tungsten carbide WC are a promising material for strengthening weldable aluminium systems Al–Si (AK type), containing 5 wt.% Si and more, which modify the silicon phase in the alloy microstructure.

Silicon presence in the quantity of up to 1 wt.% in Al-TiC system practically does not affect the interaction of titanium carbide particles with aluminium melt. Increase of silicon concentration leads to formation of titanium silicides (TiSi, TiSi,) from the liquid phase. Further increase of silicon content just enhances the interaction in this system, which can create a threat for interaction, and lead to degradation of nanosized particles of titanium carbide, when they are used as a modifying additive for welding filler materials, which contain more than 5 % Si. Therefore, superfine particles of titanium carbide will predictably be more efficient as modifiers for alloys of Al-Mg system (AMg type), where their interaction with the melt is less probable, and the reaction products do not lower the modifying effect.

The modifying additive of titanium diboride to filler materials based on aluminium alloys can be regarded as thermodynamically stable, but also such, the modifying effect of which is small, compared to other additives, studied in this work.

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