Development of phase analysis methods of impurity elements in alloys based on iron and nickel

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Abstract. Using the method of AES with ICP, new methods have been developed for quantifying the content of various forms of existence of impurity elements: Al-Al_2O_3; Zr-ZrO_2 in alloys based on iron (Fe-Sn) and nickel (Ni-Sn). Open systems were used to dissolve Al and Zr. To translate difficult-to-open aluminum oxides (corundum) and zirconium oxide (baddeleyite) into the solution, accelerated techniques were developed using the microwave system Mars 5. To confirm the completeness of the dissolution of oxides, a classical scheme of alloy fusion with alkali metal salts was used. Optimal analytical parameters for determining the elements: Al and Zr were chosen. The influence of matrix elements (iron and nickel) and methods of its elimination were studied. This made it possible to determine the elements in a wide concentration range from $1 \cdot 10^{-3}$ to n% Al and from $1 \cdot 10^{-4}$ to n% Zr without preliminary separation of the matrix with good metrological characteristics. The relative standard deviation (S_r) does not exceed 0,2. The separate determination of the contents of aluminum and aluminium oxide in the model melt of Fe-Sn-Al_2O_3 and zirconium and zirconium oxide in the Ni-Sn-ZrO_2 model melt allowed us to estimate the number of nanoparticles participating in the heterophase interaction with tin and retired to the interface in the form of ensembles and the number of nanoparticles present in the melt and affecting the crystallization process and the structure of the metal.

In metallurgy the search of new ways of improving properties of metal, including by inoculation of it with the use of nanosize powders, presents a very actual task [1]. For the study of physicochemical principles of extraction of metals from complex ores and research of interaction of exogenous refractory nanophases with capillary-active substances in the alloyed fusions of nickel and iron with the purpose of development of technological recommendations on the affinage of metal new methodologies of quantitative determination of maintenance of different forms of being of aluminium were worked out in ferrous alloys: aluminium dissolved in the metal, and aluminium in the form of corundum Al_2O_3 nanoparticles and methodologies of separate determination of amount of zirconium dissolved in the nickel, and zirconium in the form of nanoparticles ZrO_2.

Methodologies of separate quantitative determination of maintenances of different forms of existence of elements-admixtures: Al - Al_2O_3 and Zr - ZrO_2 in the alloys of the indicated composition were not found in literature. The method of atomic-emission spectrometry with the inductively-

constrained plasma (AES with ICP) was used for researches. The method is the most perspective for determination of maintenances of aluminium and zirconium, regarding of sensitivity, selectivity and metrological characteristics [2, 3]. Work was conducted on the plasma spectrometer of ULTIMA 2 firms "HORIBA JOBIN YVON" (France-Japan).

The high resolution (5 pm) of spectrometer provides the best ratio of signal to the background, which leads to low detection limits of elements. The optimal analytical parameters of determination of aluminium and zirconium were experimentally found: the discharge power - 1,2 kW; cooling argon flow is 14 l/ min; transporting is 0,80 l/ min; plasma is 0,5 l/ min; observation height 14 mm above the top turn of the induction coil; the speed rate samples is 1,0 ml/min. Analytical lengths of waves were chosen for determination of elements, that provide the suitable detection limits, a minimum of adjustments for background and overlapping of spectral lines [4]. Optimal analytical lengths of waves for determination of Al and Zr are presented in tables 1, 2. The most sensitive and selective were λ_{Al}=309,278 nm, λ_{Zr} =339,198 nm.

A significant factor is the choice of the concentration of the matrix element in the solution, which is not violated to the stability of work of the system burner - nebulizer. For iron favourable is a concentration no more than 500 ppm and for a nickel - 1000 ppm.

The possibility of determination of low concentrations of aluminium on the background of iron and zirconium on the background of nickel was by a study of the spectral interference from the base element at the scan-out of the spectrum from 190 to 800 nm. Solutions of pure iron (500 ppm) or nickel (1000 ppm) and solutions of aluminium or zirconium (5, 10, or 100 ppb) were introduced in the plasma. The detection limits of elements were estimated by the formula [5]:

$$LOD = k \cdot BEC \cdot RSD_0$$

LOD - limit of detection; k   - coefficient equal to 3 for detection limits at 3σ; BEC - the concentration of noise; RSD_0 – relative standard deviation for the zero standard.

For the evaluation of detection limits the calibration curve is built on the two points 0 and 5 ppm. The calibration is used to determine the concentration of the noise BEC. The relative standard deviation RSD_0 is determined by the results of the analysis of a zero standard during 5 minutes. As the zero calibration solution was used a standard solution of iron 500 ppm or 10000 ppm of nickel (prepared from metals of high purity). The second calibration solution was prepared on the background solution of iron 500 ppm or 10000 ppm of nickel. Concentrations of the determined elements (Al, Zr) were 5 ppm.

In tables 1, 2 are presented the calculated detection limits of aluminium and zirconium. It is seen that the detection limits of Al on the background 100 and 500 ppm of iron and Zr on a background 1000 and 10000 ppm of nickel are significantly different from those in the pure solutions and not for the better.

Table 1. Characteristics of analytical lines of aluminum.

Length wave, λ nm	Detection limit, ppb (3σ)			Interfering elements
	in pure solution	on the background		
		100 ppm Fe	500 ppm Fe	
308.215	2.0	4.5	9.0	V, Pr, Er, Ce
309.278	0.5	2.5	10.0	Nd, Tb
394.401	1.5	3.5	7.1	Pr, U, Ru, Ce
396.152	1.0	2.5	5.3	Pr, Er

Table 2. Characteristics of analytical lines of zirconium.

Length wave, λ,нм	Detection limit, ppb (3σ)			Interfering elements
	in pure solution	on the background		
		1000 ppm Ni	10000 ppm Ni	
339.198	0.02	0.05	0.10	Eu, Dy, Er, Nd, Ru, Ce
343.823	0.04	0.06	0.20	Fe, Hf, Ce, W
349.621	0.09	0.17	0.52	Nb ,Dy, Ce, Tb, Pr

The main problem of the emission analysis is to account for the influence of the matrix. On the background of iron, which is a very complex matrix, determination of trace elements is especially difficult. This is due to a temporal drift of the background, and a sophisticated form of background in area of analytical lines, and weak signal intensity. The increase in integration time reduces the detection limits, but does not decide the problem of the influence matrix. It is primarily the curvature of the calibration graphs due to significant changes of analytical signals of the elements near the limits of detection and, therefore, the deterioration of the metrological characteristics of the determination of elements. At determination of elements near-by the detection limits on their analytical signals other elements-admixtures begin to influence [6].

The influence of matrix elements (iron and nickel) and methods of their removal were studied.

On 'Figure 1' the dependences of analytical signals of different concentrations of zirconium from the concentration values of nickel are presented. The nickel content of up to 10g/l has no effect on analytical signals of solutions containing more than 2 ppb of zirconium. It does possible direct, without separation of the nickel matrix, determination of Zr beginning from $2 \cdot 10^{-4}$%. In the case of smaller concentrations of zirconium needed to make a preliminary separation of the matrix or to use methods of mathematical modeling.
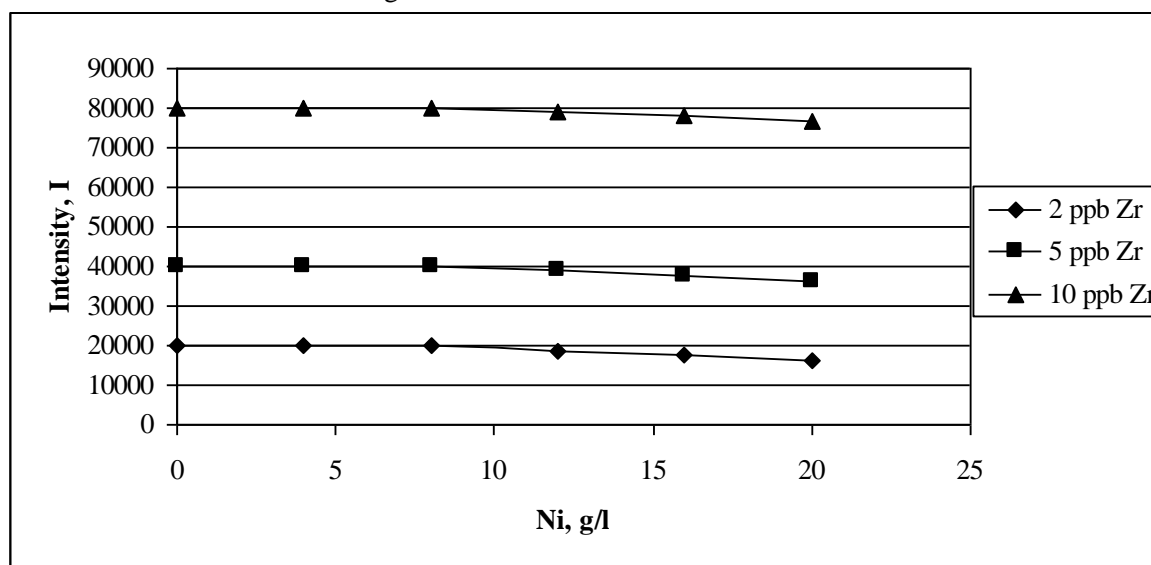
Figure 1. Matrix effect of nickel on AES with ICP determination of zirconium.
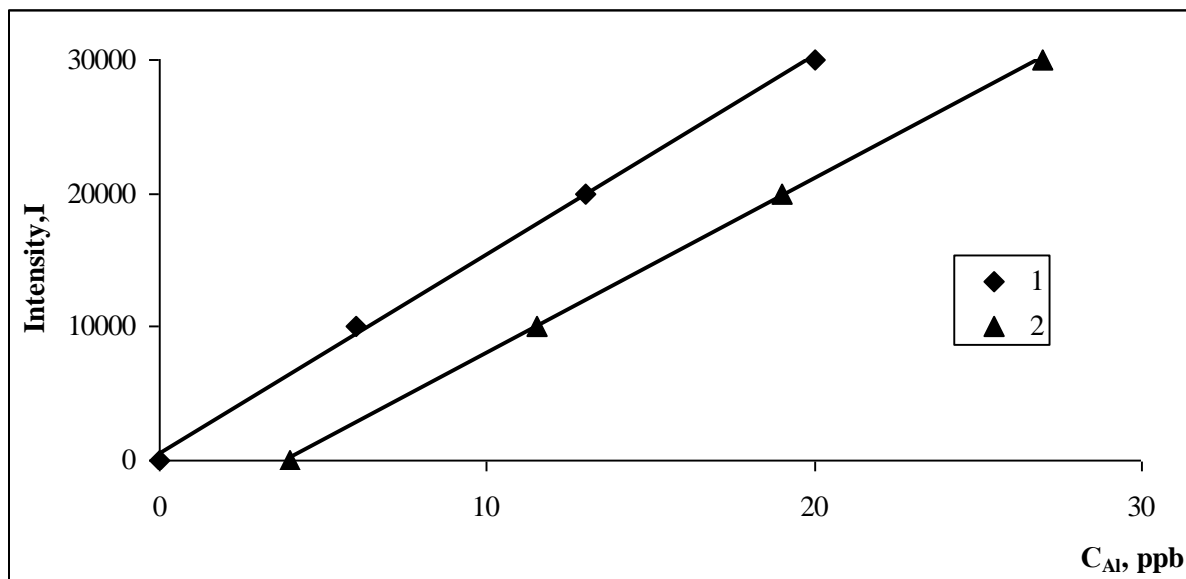
Figure 2. Calibration curves of aluminum on the background 0-100 ppm Fe (1) and on the background 500 ppm Fe (2).

On 'Figure 2' the calibration graphs for the aluminium on the background of iron from 0-100 ppm and the background 500ppm iron are shown. The calibration graphs to determine the Al for the selected analytical lines coincide for pure solutions of aluminum and containing not more than 100 ppm of iron. With the increase of iron concentration up to 500 ppm, the sensitivity of the determination of aluminium worsens and calibration curves do not coincide.

In this case it is needed to use calibration curves with the respective iron content, or to apply the method of interactive concordance of matrix [3].

The influence of the concentration of acids: HCl, HNO_3, H_2SO_4 on the analytical signals of elements were studied. On 'Figure 3' the dependences of analytical signals of Al from the nature and concentration of acid in the analyzed solution are shown. As follows from experimental data, the change in the concentration of acid in the analyzed solution leads to a change in analytical signal, and the degree of change depends on the nature and concentration of acid. So a solution of 2M HCl decreases the analytical signal Al on 3%, while the sulfuric acid of the same concentration by 11%. The increase in the concentration as HCL and HNO_3, from 0.01 M to 1 M was changed analytical signals of the elements is not more than 3%. A significant influence on the analytical signals of the elements renders the change concentrations of sulfuric acid in solution. Depressing the action of acids is due to changes in the spray system or the system of sample introduction. When you change the concentration of acid the effectiveness of spraying and, consequently, sensitivity changes. However, the practical error can be avoided by maintaining an adequate acid content in tests and standard solutions. Uncontrolled fluctuations in the concentration of acids, especially sulphuric, can lead to errors which are significantly greater than instrumental.
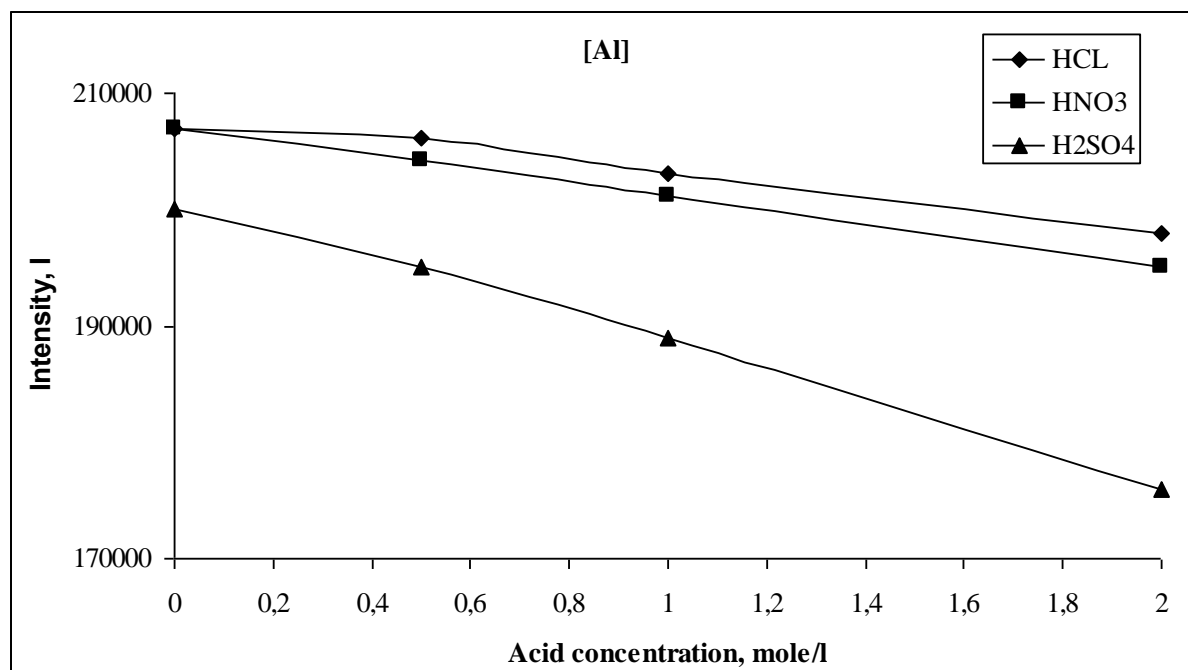
Figure 3. The dependence of the intensity of the signal Al from nature and concentration of acid.

Method AES with ICP requires translation the analyzed samples in solutions for performing analysis. All used reagents had high degree of purity. Mineral acids and their mixtures of different concentration were used for dissolution. Compositions of acids for separate translation in solution of different forms of being of elements: Al and Al_2O_3; Zr and ZrO_2 were found. In a table 3 the results of determination of aluminium are presented at the different ways of dissolution. Aluminium contained in the alloy iron in the form of Al, is easily translated into a solution with mineral acid: 10% HCl or 10 % HNO_3 at heating in glass heat-resistant open vessels. Its contents were defined at the level of 0.001%. For the conversion to a solution of Zr, dissolved in the metal, Aqua Regia (mixture concentrated HCl and HNO_3 (3:1)) was used by heating samples in open systems.

Oxides of aluminum and zirconium: corundum (Al_2O_3) and baddeleyite (ZrO_2) are some of the most difficult open connections. The dissolution of Al_2O_3 and ZrO_2 was carried out in a microwave sample preparation system MARS 5 (CEM Corporation, USA) under different conditions (P, T) of different mixtures of acids. The degree of extraction of oxides of aluminium and zirconium was studied depending on nature of solvent and time of treatment. The results are presented in tables 3, 4. Mixtures of acids for complete dissolution of samples, providing the transfer in solution of corundum (Al_2O_3) and baddeleyite (ZrO_2) were selected. Conditions of microwave exposure and temperature and time modes of decomposition of the samples were optimized. The corundum was dissolved in mixtures: HCl+ HNO_3 (1:3); HCl+ HNO_3 (3:1); HCl+ HNO_3 (1:3) + H_2O_2 and HCl+ HNO_3 (3:1) +H_2O_2 for 40 minutes at a temperature of 210^0C during realization of double cycle of autoclave microwave exposure. Baddeleyite was dissolved in a mixture of HF+ HNO_3+ HCl (4:3:1) for 40 minutes at a temperature of 210^0C when conducting a triple cycle of the autoclave microwave exposure.

The fullness of being transferred into a solution of oxides of aluminum and zirconium with found mixtures was controlled by the classical method: by converting Al_2O_3 and ZrO_2 into solution after melting of samples with salts of alkali metals [6]. Similar results for the determination of aluminium and zirconium contents were received in the solution obtained after dissolution of the samples in the MARS 5 system and after fusing. The use of modern autoclave sample preparation for dissolution with acids is preferable to the classic melting, since the time of analysis decreases, and most importantly,

the metrological characteristics of the determination of elements improve. When using fusion with the oxides and salts of alkali metals the detection limits of elements deteriorate for two reasons: the value of the blank experience increases dramatically and the presence of large concentrations of alkali metals in solution adversely affects on the analytical signals of the determined elements in spectroscopic methods of analysis. According to the developed methods of sample dissolution in the microwave sample preparation system MARS 5 obtained solutions were analyzed. The total content of zirconium does not exceed 0.3%, and aluminum of 0,03% (table. 3, 4). These values are fundamentally different from the results obtained after dissolution of samples in open systems.

Table 3. The results of AES-ICP determination of the content of various forms of existence of aluminium in alloys based on iron using different methods of dissolution

Dissolution method samples	Mixtures for dissolution	Conditions of dissolution	Content of Al, %	S_r
Dissolution in open vessels	10% HCl	Heating in heat-resistant glass dish	0.0011	0.2
	10 % HNO_3		0.0012	0.2
	HCl		0.0010	0.2
	HNO_3		0.0009	0.2
	50 % HCl		0.0012	0.2
	50 % HNO_3		0.0010	0.2
	$HCl+H_2O_2$		0.0012	0.2
	$HNO_3+H_2O_2$		0.0012	0.2
	$HCl+HNO_3$ (1:3)		0.0011	0.2
	$HCl +HNO_3$ (3:1)		0.0013	0.2
	$HCl + HNO_3$ (1:3) $+H_2O_2$		0.0013	0.2
	$HCl +HNO_3$ (3:1) $+H_2O_2$		0.0012	0.2
Dissolution in closed autoclave microwave system Mars5	10% HCl	210 °C 40 min.	0.0015	0.2
	10 % HNO_3		0.0019	0.2
	HCl		0.0019	0.2
	$HNO_{3конц}$		0.0020	0.2
	50 % HCl		0.0021	0.2
	50 % HNO_3		0.0022	0.2
	$HCl+H_2O_2$		0.0073	0.2
	$HNO_3+H_2O_2$		0.0081	0.2
	$HCl + HNO_3$ (1:3)		0.028	0.04
	$HCl + HNO_3$ (3:1)		0.029	0.04
	$HCl +HNO_3$ (1:3) $+H_2O_2$		0.030	0.04
	$HCl + HNO_3$ (3:1) $+H_2O_2$		0.029	0.04
Fusion	Na_2CO_3	Pt crucible, 1000-1200 °C 10-20 min.	0.021	0.06
	$Na_2CO_3+Na_2B_4O_7$		0.030	0.05
	$LiBO_2$		0.028	0.05

Table 4. The results of AES-ICP determination of the content of various species of zirconium in alloys based on nickel using of different methods of dissolution

Dissolution method samples	Mixtures for dissolution	Conditions dissolution	Content of Zr, %	S_r
Dissolution in open vessels	HCl HNO_3 H_2SO_4 $HCl+HNO_3$ (3:1) $HCl+HNO_3$ (3:1) + H_2O_2 $H_2SO_4+HNO_3$ (1:1)	Heating in heat-resistant glass dish	0.0008 0.0009 0.0008 0.0030 0.0029 0.0030	0.2 0.2 0.2 0.2 0.2 0.2
Dissolution in closed autoclave microwave system Mars5	$HCl+HNO_3$ +HF (1:3:4) $H_2SO_4+HNO_3$ (1:1) $HCl+HNO_3$ (3:1) + H_2O_2	210 °C 45 min	0.29 0.0030 0.0030	0,04 0,2 0,2
Fusion	Na_2CO_3 $Na_2CO_3 + Na_2B_4O_7$ $LiBO_2$	Pt crucible, 1000-1200 °C 10-20 min	0.22 0.30 0.28	0.06 0.05 0.05

Due to the lack of standard samples of composition of studied materials to confirm the obtained results for the determination of aluminium and zirconium by means of methods AES with ICP were compared with the data of the method of atomic absorption spectrometry and mass spectrometry with inductively coupled plasma (tables 5, 6). A good convergence of the results of determination by different methods confirms the correctness of determination of Al and Zr by the method of AES with ICP.

Table 5. The results of determination of aluminium by various methods.

Method of sample preparation		AES-ICP $\lambda = 309,278$ нм			AAC (flameN$_2$O+C$_2$H$_2$) $\lambda = 309,3$ нм		
		Limit of detection Al, ppb (3σ)	Al, %	S_r	Limit of detection Al, ppb (3σ)	Al, %	S_r
Acid dissolution (autoclave microwave system Mars5)	1) 100 ppm Fe	2.5	0.030	0.04	5.0	0.031	0.06
	2) 500 ppm Fe	10.0	0.028	0.12	10.0	0.028	0.10
Fusion with $Na_2CO_3 + Na_2B_4O_7$	1) 100 ppm Na	9.5	0.031	0.10	15	0.031	0.12
	2) 500 ppm Na	25.0	0.028	0.22	50	0.028	0.25

Table 6. The results of determination of various forms of elements (n=10, P=0,95)

The matrix composition of the sample	Define form elements	Methods of translation of of sample into the solution	Mass contents of the elements, %	
			The method of analysis	
			AES-ICP	AAS, MS-ICP
Fe	Al	Open system: HCl	0.0013	0.0011
	Al_2O_3 (corundum)	Microwave autoclave system MARS 5: HCl+HNO$_3$	0.031	0.033
		Fusion with Na$_2$CO$_3$	0.032	0.034
Ni	Zr	Open system: HCl+HNO$_3$+HF	0.0052	0.0056
		Fusion with Na$_2$O$_2$	0.21	0.22
	ZrO_2 (baddeleyite)	Microwave autoclave system MARS 5: HNO$_3$+HF+H$_2$O$_2$	0.22	0.23

Conclusions:

1. Using the method AES with ICP a new express methods of phase analysis of systems were developed:

- aluminium, dissolved in the doped alloy of iron and nanoparticles of Al_2O_3 in the form of corundum,

- zirconium dissolved in the doped alloy of nickel and ZrO_2 nanoparticles in the form of baddeleyite.

2. New methods for rapid dissolution of corundum and baddeleyite with using the autoclave microwave system Mars 5 were developed.

The proposed methods allowed to determine the content of various forms of aluminum, beginning from $n \cdot 10^{-3}$ % and zirconium, beginning from $n \cdot 10^{-4}$ % and above without prior separation of matrix with good metrological characteristics. The relative standard deviation (S_r) does not exceed 0,2.

3. Separate determination of the contents of aluminum and aluminum oxide in a model molten Fe-Sn-Al_2O_3 and zirconium and zirconium oxide in the model melt of the Ni-Sn-ZrO_2 made it possible to assess the number of nanoparticles involved in heterophase interaction with the tin, and retired to the phase interface in the form of bands and the number of nanoparticles present in the melt and affect the crystallization process and the structure of the metal.

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