УДК 669.0171/543.063 https://doi.org/10.51301/vest.su.2021.i2.19

G.M. Ibrayeva*, B.M. Sukurov
Institute of Metallurgy and Ore Beneficiation, Satbayev University, Almaty, Kazakhstan
*e-mail: gm.ibrayeva@gmail.com

PECULIARITIES OF MICROSTRUCTURE OF REACTIVE DIFFUSION ZONE IN Al-Co SYSTEM

Abstract. Microstructure and element composition of sample having the multilayer reactive diffusion zone (RDZ) in Al-Co system obtained by means of contact smelting at 1375 °C for 1 hour were studied in cross-section by means of scanning electron microscopy and electron probe microanalysis (SEM-EPMA). In the multilayer RDZ the following intermetallic compounds $CoAl_3$, Co_2Al_5, CoAl, β' + (αCo), as well as solid solution of CoAl in (αCo) were identified using the spot energy-dispersion analysis (EDS). Using the methods of linear EDS and wave-dispersion (WDS) analyses the profiles of element concentrations were obtained. These concentration profiles indicate that $CoAl_3$, Co_2Al_5, CoAl and β' + (αCo) are able to form solid solutions in each other. Microstructural peculiarities of RDZ forming in the layers $CoAl_3$, Co_2Al_5, CoAl and β' + (αCo) can simulate the actual structural pattern of Al-Co alloys (as-cast).

Keywords: intermetallics, diffusion, joining, microstructure, interfaces, scanning, electron microscopy

Introduction. The behaviour of microstructure in the multilayer reactive diffusion zone (RDZ) forming in binary metal systems assists to disclose interaction between the intermetallic compounds at different thermodynamic conditions. The general idea for contact smelting for binary metal system (or diffusion couples technique) is based on expectations of appearance of all compounds existing in the corresponding equilibrium diagram in the same sequence at the given temperature. The term “reactive diffusion zone“ logically joints two separate meanings “diffusion zone” and “reaction zone“ because diffusion transmission of atoms and phase transformation resulting to the certain phase composition can occur not only due to physical processes, but due to chemical processes too [1][2][3][4]. In the most of binary and more complex metal systems the diffusion is accompanied not only by the formation of unlimited solid solutions based on main components in sample, but also by the formation of phases including the mixtures of solid solutions existing in limited range of concentrations and intermetallic phases [3]. For these cases the special opportunities can be appeared in evaluation of fragments of diagrams through measuring of component concentrations in each layer.

The change of these concentrations along the cross-section of sample of binary system can clarify the RDZ fine structure where intermetallic compounds are clearly observed in form of layers. It is obviously that concentration jumps between layers should correspond to the interfaces of single-phase areas according to equilibrium diagram. To obtain the data on element concentrations along to RDZ cross-section it will be reasonably to apply the spot microprobe analysis to observed intermetallic compounds. It is typical that atomic per cent of registered elements are undoubtedly recognized as fractions of phase components of compounds. The linear profiles of element concentrations for binary systems in the standard model of reactive diffusion were considered in [2] [3].

Experimental procedure. The Al-Co system has been selected since its compounds nowadays represent the serious practical interest [5]. The technique of contact smelting was used to obtain RDZ cross-section in Al-Co system [6] [7]. The samples were obtained at temperature 1375 °C for 1 hour. High purity aluminium (99.99 % Al) and cobalt (99.98 % Co) were used as initial materials. For sample preparation Secotom-50 and Tegramin (STRUERS) were used. Microstructural studies were performed using the electron probe microanalyzer JXA-8230 (JEOL) equipped with energy-dispersion spectrometer (EDS) and wave-dispersion spectrometer (WDS) controlled by EPMA software. To reduce dispersion of values for spot EDS-analysis the areas having the uniform contrast in backscattered electron image were selected. At these conditions the statistical error in the measurements of component concentrations was not higher ± 0.05%. Electron probe current was selected in range 4-5.3 nA to keep the dead time not higher than 15% for EDS-analysis, and did not exceed 10 nA for WDS linear analysis.

Results and discussion. In contact area of components of Al-Co system the multilayer RDZ is formed. According to equilibrium diagram the formed layers are the possible products of peritectic reactions. The details of cross-section sequence of phase formation in the Al-Co system for different temperatures are described in [7]. The resulted intermetallic compounds were identified through the spot measurements using EDS-analysis and comparison the concentrations of their components with reference values. The following intermetallic compounds having constant compositions were found: $CoAl_3$, Co_2Al_5, CoAl, β' + (αCo), and solid solution CoAl in (αCo). The example of this microstructure with the layers having the different contrast in mode of backscattered electrons is shown in Fig. 1.

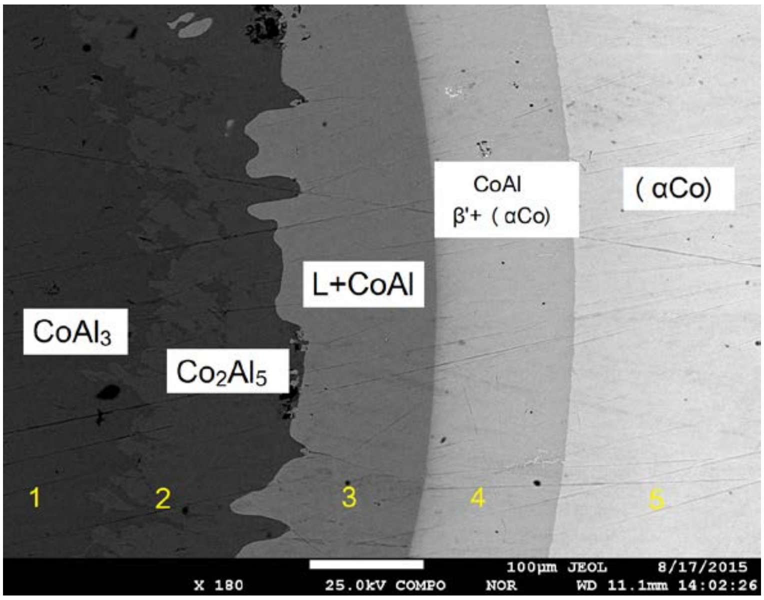

Fig. 1. Multilayer microstructure of RDZ in Al-Co smelted couple

The concentration ranges of RDZ layers are shown in Table 1.

Table 1. **The concentration compositions and corresponding phases**

Layer in RDZ	Experimental at.% Co	A.J. McAlister [8], at.% Co	Compound	Temperature range, °C [8] [9]
1	25.50-29.18	25.6	$CoAl_3$	1135-200
2	28.72-31.86	28.6	Co_2Al_5	1180-200
3	35.76-51.79	~48-78,5	L+CoAl	1170-1135
4	57.38-78.83	78.5-84.4	CoAl β' + (αCo)	1375-1180
5	77.39-97.39	84-100	αCo	1640-1400

Different stoichiometric proportions of concentrations from CoAl to $CoAl_3$ are consistent with the data taken from equilibrium diagram [9] [10]. Cobalt concentration of Layer #4 can be considered as an example of such identification. Since its range was about 78.5-84.4 at.% Co it is undoubtedly corresponds the solid solution β' + (αCo) at temperature 1400°C according to updated data [10]. Another peculiarity of this microstructure is that “pure” Al area was not detected. It means that all aluminium has been reacted to the extent that even there wasn't a solid solution Co/Al. The next worthwhile structural peculiarity of Al-Co binary system in cross section is that the contacts between the layers $CoAl_3$, Co_2Al_5, and CoAl simulate the real structural pattern observed in Al-30.5Co alloy in "as-cast" condition [10, Fig.2 c]. In particular in this above-mentioned work no direct contacts were observed between $CoAl_3$ and CoAl phases; in our experiment between these layers obtained by means of contact smelting do not have direct contacts too.

Application of linear microanalyses to the same area permitted to reveal some features of component concentration profiles. Their changes occur not only in form of "jumps" at interfaces between layers, but also in form smooth and monotonic raising or decreasing within each layer. Figure 2 shows how the EDS and WDS linear concentration profiles for the same layers of system Al-Co coincide in every detail at their "sharp" and "smooth" fragments.

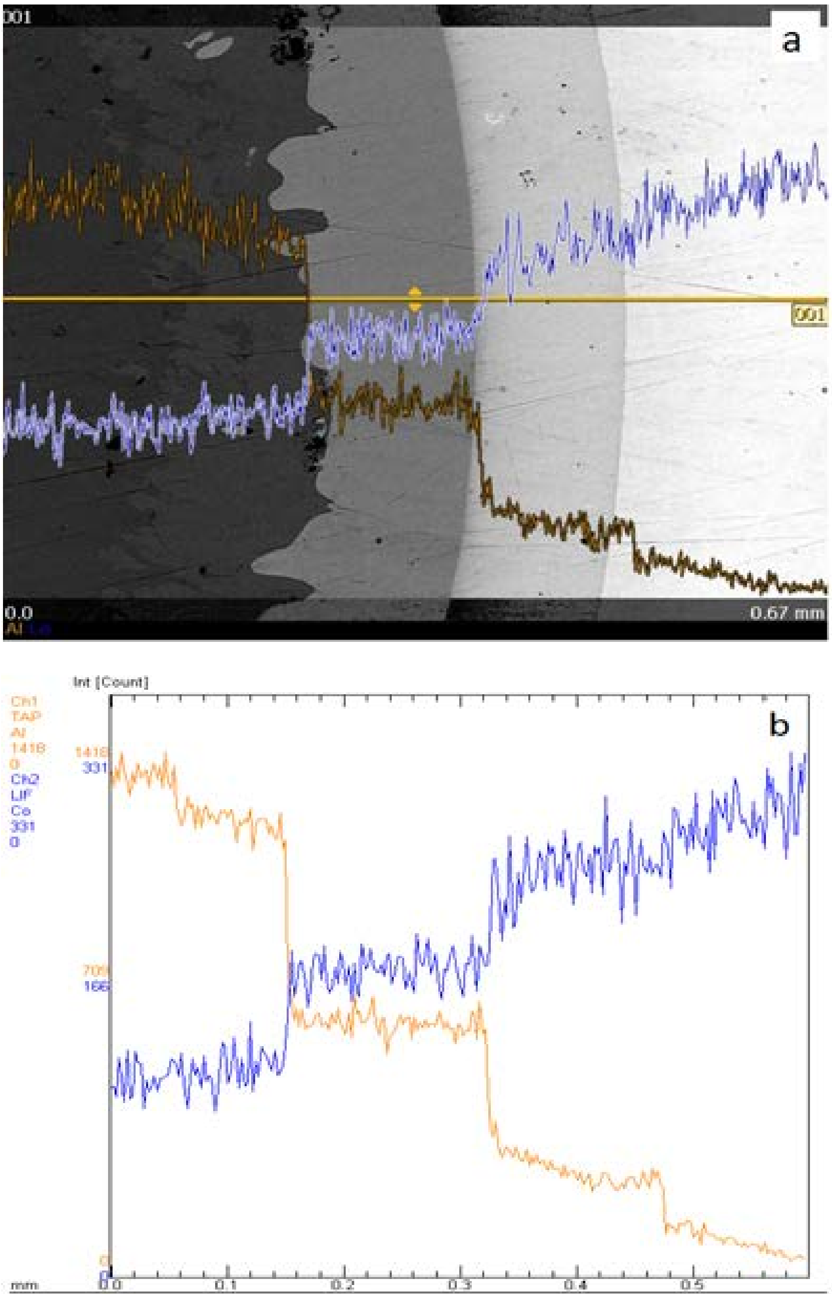

Fig. 2. Concentration profiles of Co (blue) and Al (yellow) in multilayer RDZ (a) EDS (b) WDS

The similar behaviour of concentration profile was observed in very thin contact formed in Al-Ni system [11] (Fig.5). It is very important to know the discrepancies from stoichiometric composition, e.g. in case Al-Ni system there was established the direct relation between them and mechanical properties [4].

Comparison of Table 1 and Figure 2 demonstrates that small raise of Co concentration at layer $CoAl_3$ results to appearance of Co_2Al_5. One can note that for this area the slope of the concentration profile is insignificant since the difference is about 2-3 at.% only. The similar behaviour is observed on transition of β' + (αCo) to solid solution, but here the slope of concentration profile is more sharp compared to previous fragment. For binary systems it can be attributed to ability to create solid solutions up to threshold concentrations. On the interfaces between compounds CoAl and β' + (αCo) and between Co_2Al_5 and CoAl one can observe concentration profiles having other slopes. These experimental results can be treated that above-mentioned compounds $CoAl_3$, Co_2Al_5, CoAl, and β' + (αCo) create solid solution in each other.

From above-mentioned observations it is clearly seen that concentration composition of each layer corresponds to certain phase and varies in the limits of concentrations of well-known phases. Therefore the slow cooling of sample from 1375 °C resulted to RDZ having 5 layers. The first Layer (nearly invisible) corresponds to concentration composition of $CoAl_3$. According to [8] during the cooling from higher temperatures to 1090°C it is formed at concentrations up to25.6 at.% Co. The interface between the first and second Layers has formed as festoons. The concentration composition of the second Layer corresponds to Co_2Al_5. The interface between the second and third Layers keeps its form as festoons. The third Layer having pronounced contrast and interfaces corresponds to concentration of mixture Co_2Al_5+CoAl. Interfaces are observed as the smooth curves. The fourth and fifth Layers have the common matrix (αCo), moreover in the fourth Layer it is diluted with compound CoAl having the corresponding Co concentration. Thus it is solid solution on the base of CoAl in (αCo), which has different designations ξ or β' in different sources.

In our experiment the following phases described in equilibrium diagram [9] were not observed:

Co_2Al_9 —18.1at.% Co, 970°C, and

Co_4Al_{13}—23.5 at.% Co, 1093°C.

It may be related to their suppression by adjacent compounds in this geometry, i.e. these stoichiometric compositions became unachievable ones. In our case due to high temperature and short period of exposure the non-equilibrium conditions for formation of these compounds were obviously occurred. The main idea is that non-equilibrium conditions can result to local deviations from stoichiometric compositions.

Conclusion. The multilayer microstructure of RDZ obtained in binary Al-Co system due to contact smelting and thermal exposure at 1375°C for 1 hour has been studied by means of SEM-EPMA methods. The layers of intermetallic compounds and solid solutions were identified on the base of comparison of experimental results with referral ones as follows $CoAl_3$, Co_2Al_5, CoAl, and β' + (αCo). From the behaviour of component concentration profiles in cross-section there was established that above-mentioned intermetallic compounds create solid solutions in each other. The structural peculiarities of RDZ in binary Al-Co system can partially simulate the real structural pattern of Al-30.5Co alloy in "as-cast" condition.

This work has been implemented in the framework of Governmental Order of Kazakhstan on Program "Grant Funding of Scientific Research (Grant № 203/1 №1196/GF4) "Creation of the fundamentals of the technology for the production of high-strength and heat-resistant intermetallic superalloys based on aluminides by powder metallurgy (2015-2017)"

Acknowledgments. Authors express their acknowledgments to Prof. Valery N. Volodin, Doctor Physical-Mathematical Sciences and Doctor of Technical Sciences, and Aleksander V. Panichkin, Candidate of Technical Sciences, from Institute of Metallurgy and Ore Beneficiation, Satbayev University (Kazakhstan, Almaty) for valuable comments and notes.

REFERENCES

[1] Sauthoff G. Intermetallics // Weinheim. New York. Basel. Cambridge. Tokyo. VCH. 1995. – P.423 https://doi.org/10.1002/14356007.e14_e01.pub2

[2] Kodentsov A.A., Bastin G.F., Van Loo F.J.J. The diffusion couple technique in phase diagram determination. J. Alloys and Compounds. 2001; 2; 207–217; https://doi.org/10.1016/S0925-8388(00)011487-0

[3] Gusak A., Storozhuk N. Diffusion-Controlled Phase Transformations in Open Systems. Handbook of Solid State Diffusion, 2017; 2, 37–100. https://doi.org/10.1016/b978-0-12-804548-0.00002-5

[4] Oskay C., Rudolphi M., Affeldt E.E., Schütze M., Galetz M.C. Evolution of microstructure and mechanical properties of NiAl-Diffusion coatings after thermocyclic exposure. Intermetallics. 2017; 89; 22–31; https://doi.org/10.1016/j.intermet.2017.05.012

[5] Lekatou A., Sfikas A. K., Petsa C., Karantzalis A.E. Al-Co Alloys Prepared by Vacuum Arc Melting: Correlating Microstructure Evolution and Aqueous Corrosion Behavior with Co Content. Metals. 2016; 6; 46; https://doi.org/10.3390/met6030046

[6] Kodentsov A., Paul A. Diffusion Couple Technique: A Research Tool in Materials Science. Handbook of Solid State Diffusion, 2017; 2; 207–275. https://doi.org/10.1016/b978-0-12-804548-0.00006-2

[7] Ibraeva G. M., Sukurov B.M., Aubakirova R. K., Mansurov Yu. N. Multilayer structure formed in diffusion zone of Al-Co and Al-Ni system, News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences. 2018; 3; 57-63.

[8] McAlister A.J., The Al-Co (Aluminum-Cobalt) System. Bulletin of Alloy Phase Diagrams. 1989; 10; 6; 646- 650; https://doi.org/10.1007/BF02877635

[9] Predel B., Madelung O. Springer Materials Al-Co (Aluminum-Cobalt) Landolt-Börnstein - Group IV Physical Chemistry 5A (Ac-Au – Au-Zr) 1991; http://materials.springer.com/lb/docs/sm_lbs_978-3-540-39444-0_97 10.1007/10000866_97

[10] Stein F., He C., Dupin N. Melting behaviour and homogeneity range of B2 CoAl and updated thermodynamic description of the Al-Co system. Intermetallics. 2013; 39; 58-68. https://doi.org/10.1016/j.intermet.2013.03.011

[11] Krasnowski M., Gierlotka S., Kulik T. Nanocrystalline matrix Al3Ni2–Al–Al3Ni composites produced by reactive hot-pressing of milled powders. Intermetallics. 2014; 54; 193–198. https://doi:10.1016/j.intermet.2014.06.012

Г.М. Ибраева*, Б.М. Сукуров

Институт металлургии и обогащения, Satbayev University, Алматы, Казахстан

*e-mail: gm.ibrayeva@gmail.com

ОСОБЕННОСТИ МИКРОСТРУКТУРЫ ЗОНЫ РЕАКЦИИ И ДИФФУЗИИ В СИСТЕМЕ Al-Co

Аннотация. Микроструктура и элементный состав образца, имеющего многослойную зону в реакционной диффузии (РДЗ) в системе Al-Co, полученного контактным плавлением при 1375 °С в течение 1 часа, исследовали в поперечном сечении методами растровой электронной микроскопии и электронно-зондового микроанализа (РЭМ-РСМА). В многослойной РДЗ с помощью точечного энергодисперсионного анализа (EDS) были идентифицированы следующие интерметаллиды $CoAl_3$, Co_2Al_5, CoAl, β '+ (αCo), а также твердый раствор CoAl в (αCo). С помощью методов линейного EDS и волнового дисперсионного анализа (WDS) были получены профили концентраций элементов. Эти профили концентрации показывают, что $CoAl_3$, Co_2Al_5, CoAl и β '+ (αCo) способны образовывать твердые растворы друг в друге. Микроструктурные особенности образования РДЗ в слоях $CoAl_3$, Co_2Al_5, CoAl и β '+ (αCo) могут моделировать реальный структурный рисунок сплавов Al-Co (в литом состоянии).

Ключевые слова: интерметаллиды, диффузия, металлические соединения, микроструктура, интерфейсы, сканирующая электронная микроскопия.

Г.М. Ибраева*, Б.М. Сукуров
Металлургия және кен байыту институты, Satbayev University, Алматы, Қазақстан
*e-mail: gm.ibrayeva@gmail.com

Al-Co ЖҮЙЕСІНДЕГІ РЕАКЦИЯ ЖӘНЕ ДИФФУЗИЯ АЙМАҒЫНЫҢ МИКРОҚҰРЫЛЫМДЫҚ ЕРЕКШЕЛІКТЕРІ

Аңдатпа. 1375 °C температурада жанасу арқылы 1 сағат ішінде алынған Al-Co жүйесіндегі көп қабатты реакциялық диффузиялық аймағы (РДА) бар үлгінің микроқұрылымы мен элементтік құрамы көлденең қимада сканерлеу арқылы электронды микроскопия және электронды зондты микроталдау арқылы зерттелді. Келесі металларалық қосылыстар $CoAl_3$, Co_2Al_5, CoAl, β '+ (αCo), сондай-ақ (αCo) -да CoAl-дің қатты ерітіндісі көп қабатты РДА-да нүктелік энерго дисперсиялық талдауды (EDS) қолдану арқылы анықталды. Элемент концентрациясы профильдері сызықтық және дисперсияның толқындық талдау (WDS) көмегімен алынды. Бұл концентрация профильдері $CoAl_3$, Co_2Al_5, CoAl және β '+ (αCo) бір-бірінде қатты ерітінділер түзуге қабілетті екенін көрсетеді. $CoAl_3$, Co_2Al_5, CoAl және β '+ (αCo) қабаттарындағы РДА түзілуінің микроқұрылымдық ерекшеліктері Al-Co қорытпаларының нақты құрылымдық үлгісін (құйылған күйінде) ұқсата алады.

Негізгі сөздер: интерметаллидтер, диффузия, металларалық қосылыстар, микроқұрылым, фаза шегі, растр электронды микроскопиясы.