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Determination of the thermodynamic properties for Cr–Co–Me (Me = Mo, Al) systems by using the general solution model for predicting

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The results of the determination of the thermodynamic properties for ternary systems Cr–Co–Me (Me = Mo, Al) using a new general solution model for the predictions are presented in this work. For five sections (with mole ratio Co : Me = 2:8, 4:6, 5:5, 6:4, 8:2) investigated in each ternary system at temperature of 2000 K, integral molar excess Gibbs energies and partial molar thermodynamic properties of chromium were calculated.

Keywords: alloy thermodynamics, thermodynamic predicting, ternary systems, Cr-Co-Mo system, Cr-Co-Al system

Alloys based on the Cr–Co–Me (Me = Mo, Al) systems are of great practical interest in the production of Ni-based super alloys,1-5 surgical implants,[6–8] as well as heat-resistant and corrosion-resistant protective coatings.[9–11]

In spite of this fact, thermodynamic analysis of such multicomponent systems has not yet been reported in the literature, while there are a lot of articles dealing with the thermodynamics of the constituent binary systems.[12–18] The reasons are experimental difficulties, especially the high investigation temperatures required.

Having in mind such problems, it is anticipated that most of the thermodynamic data of ternary and multicomponent systems will come from theoretical calculations rather than from direct experimentation. Hence, a new general solution model for the prediction of the thermodynamic properties of multicomponent systems from binaries has been presented recently in the literature.[19] It is simple, effective and employs more reliable binary sources that are easily obtained either experimentally or theoretically.

In order to contribute to a better knowledge of the Cr–Co–Mo and Cr–Co–Al thermodynamics, the results of the application of the new general solution model are presented in this paper.

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THEORETICAL BACKGROUND

Traditional predicting models for the representation of ternary thermodynamic properties, based on the three corresponding binary systems, are classified according to Hillert[20] into two categories: symmetrical (Kohler, Muggianu) and asymmetrical (Toop, Hillert).

Recently, a general solution model was suggested by Chou,[19] which breaks down the boundary between the symmetrical and asymmetrical models, which has already been proved in some practical examples[19,21,22] as a correct and accurate model.

In the application of the Chou's model, first of all, it is neccessary to calculate the similarity coefficients for three binaries, which are defined as:[19]

$$x_{i(ij)}^{<k>} = \frac{\eta(ij, ik)}{\eta(ij, ik) + \eta(ji, jk)} \qquad (i, j, k = 1,2,3,\ i \neq j \neq k) \tag{1}$$

where η (ij, ik) is a function related to the excess Gibbs energy of "ij" and "ik" binaries:

$$\eta(ij, ik) = \int_{x_i=0}^{x_i=1} (\Delta G_{ij}^{xs} - \Delta G_{ik}^{xs})^2 \, dX_i \; ; \; X_i = X_{i(ij)} = X_{i(ik)} \tag{2}$$

and called as the deviation sum of squares. Thus, the selected binary compositions $X_{i(ij)}$ can be calculated in terms of the ternary composition x_i:

$$X_{i(ij)} = x_i + x_k \, x_{i(ij)}^{<k>} \tag{3}$$

Fig. 1 shows the selected binary comoposition points of the Chou's new model. The major difference between this model and the current models is that, the selected binary composition points for this new model are closely related to the ternary system considered and can change within a range depending on the characteristics of ternary system.

So, the integral molar excess Gibbs energy for the ternary system, according to the Chou's general solution model, is expressed by:

$$\Delta G^{xs} = W_{12}\Delta G_{12}^{xs} + W_{23}\Delta G_{23}^{xs} + W_{31}\Delta G_{31}^{xs} \tag{4}$$

where the probability weight W_{ij} is defined as:

$$W_{ij} = \frac{x_i \, x_j}{X_{i(ij)} X_{j(ij)}} \tag{5}$$

Therefore, when the three binary integral molar excess Gibbs energies are known, one may calculate the ternary integral molar excess Gibbs energy based on the equations given. If the binary integral molar excess Gibbs energy is given in terms of the regular solution parameters, the above calculation can be simplified to:

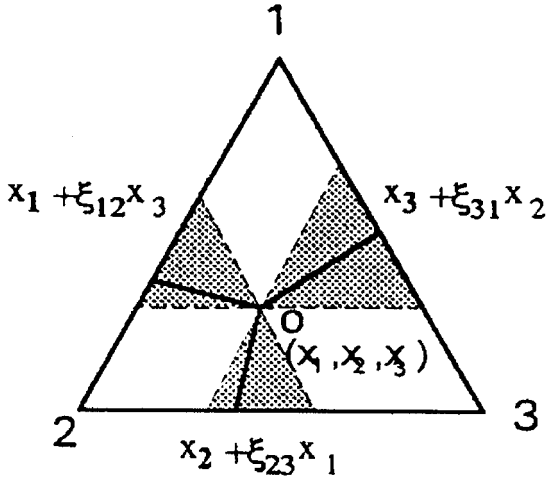

Fig. 1. The selected binary composition points for the Chou's model[19].

$$\Delta G^{xs} = x_1x_2(A^0_{12} + A^1_{12}(x_1 - x_2) + A^2_{12}(x_1 - x_2)^2) + x_2x_3(A^0_{23} + A^1_{23}(x_2 - x_3) + A^2_{23}(x_2 - x_3)^2) + x_3x_1(A^0_{31} + A^1_{31}(x_3 - x_1) + A^2_{31}(x_3 - x_1)^2) + f x_1x_2x_3 \quad (6)$$

where A^0_{ij}, A^1_{ij}, A^2_{ij} are regular-solution parameters for the binary system "ij" independent of compositon, depending only on temperature:

$$\Delta G^{xs}_{ij} = X_iX_j(A^0_{ij} + A^1_{ij}(X_i - X_j) + A^2_{ij}(X_i - X_j)^2 + \ldots + A^n_{ij}(X_i - X_j)^2) \quad (7)$$

where X_i and X_j indicate, respectively, the mole fraction of compoonent "i" and "j" in the "ij" binary system. The function f is the ternary interaction coefficient expressed by

$$f = (2x_{12} - 1)A^2_{12}((2x_{12} - 1)x_3 + 2(x_1 - x_2)) + A^1_{12} + (2x_{23} - 1)A^2_{23}((3x_{23} - 1)x_1 + 2(x_2 - x_3) + A^1_{23}) + (2x_{31} - 1)A^2_{31}((2x_{31} - 1)x_2 + 2(x_3 - x_1)) + A^1_{31} \quad (8)$$

In all the given equations, ΔG^{xs} and $\Delta G_{ij}{}^{xs}$ correspond to the integral molar excess free energies for ternary and binary systems, respectively, while x_1, x_2, x_3 represent the mole fraction of the comoponents in the investigated ternary system.

RESULTS AND DISCUSSION

The thermodynamic calculations in the ternary systems Cr–Co–Mo and Cr–Co–Al were performed along the lines of a constant Co:Mo and Co:Al mole ratio, respectively. These ratios for the selected five cross sections in the investigated systems are given in Table I.

The data necessary for the calculation according to the Chou model[19] were taken from the articles by Kaufman and Nesor.[12–14] The binary regular-solution parameters for the constitutional binaries in the investigated ternary Cr–Co–Mo and

Cr–Co–Al systems are presented in Table II, while the calculated values for the integral excess Gibbs energies for these systems, at the investigated temperature of 2000 K, are given in Table III.

TABLE I. Investigated cross sections in the ternary systems Cr–Co–Mo and Cr–Co–Al

Sections	A	B	X	C	D
Co:Me, Me = Mo, Al (mole ratio)	2:8	4:6	5:5	6:4	8:2

TABLE II. Binary regular-solution parameters for the constitutional binaries in the ternary systems Cr–Co–Mo and Cr–Co–Al

Systems *i-j*	$A_{ij}^0(T)$	$A_{ij}^1(T)$
Cr–Co	–8368	0
C–Mo	2510	0
Cr–Mo	19037–8.58 *T*	6485–2.72 *T*
Co–Al	–281347+118.003T	174264+0.379T+0.03612T2
Cr–Al	–46442	0

TABLE III. Integral excess Gibbs energies for the constitutional binaries in the investigated ternary systems at the temperature of 2000 K calculated from the equation:[19] $\Delta G^{xs}_{ij} = X_{i(ij)}X_{j(ij)}(A_{ij}^0(T) + + A_{ij}^1(T)(X_i–X_j))$, (in J/mol)

x_i	System *i-j*				
	Cr–Co	Co–Mo	Cr–Mo	Co–Al	Cr-Al
0.1	–753	226	94	–27085	–4180
0.2	–1339	402	200	–37927	–7431
0.3	–1757	527	306	–36360	–9753
0.4	–2008	602	400	–26218	–11146
0.5	–2092	628	469	–11335	–11611
0.6	–2008	602	501	4454	–11146
0.7	–1757	527	482	17317	–9753
0.8	–1339	402	401	23418	–7431
0.9	–753	226	244	18923	–4180

Based on these starting data, similarity coefficients were determined from Eq. (1) and their values are:

— for the Cr–Co–Mo system: $\chi_{Cr–Co} = 0.470$, $\chi_{Co–Mo} = 0.997$ and $\chi_{Mo–Cr} = 0.004$

— for the Cr–Co–Al system: $\chi_{Cr–Co} = 0.083$, $\chi_{Co–Al} = 0.910$ and $\chi_{Al–Cr} = 0.522$, which indicates that both in investigated systems are, according to Hillert's classification, 20 assymetrical systems.

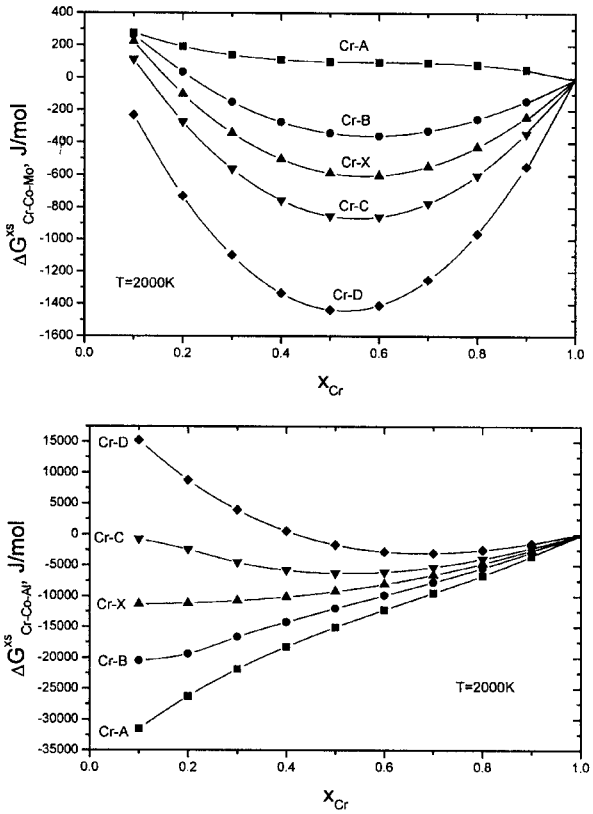

Fig. 2. The dependence of the integral excess Gibbs energy on composition for both the investigated systems at 2000 K.

Further calculations were carried out for 45 alloys in all of the selected cross sections in each of the investigated ternary system at the temperature of 2000 K, according to the fundamentals of the general solution model, as given by Eqs. (6,8). The results of the thermodynamic predictions for the Cr–Co–Mo and Cr–Co–Al systems are given in Table IV, while the graphic illustration of the dependence of the integral excess Gibbs energy on composition, for both investigated systems, is shown in Fig. 2.

The partial molar excess Gibbs energies for chromium in all the investigated sections of the Cr–Co–Mo and Cr–Co–Al systems at the temperature of 2000 K were determined according to the known integral molar excess Gibbs energies using the following relation:[23]

$$G^{xs}_{Cr} = DG^{xs} + (1 - x_{Cr})(\P DG^{xs}/\P x_{Cr}) \quad (9)$$

The calculated values for the chromium partial molar excess Gibbs energies, activity coefficients and activities, required for a complete thermodynamic description of the Cr–Co–Mo and Cr–Co–Al alloy systems, are presented in Table V, while the dependence of the chromium activity on composition is graphicaly presented in Fig. 3.

TABLE IV. Integral excess Gibbs energies, ΔG^{xs} (in J/mol), for the systems Cr–Co–Mo and Cr–Co–Al at the temperature of 2000 K

xCr	Co–Cr–Mo					Co–Cr–Al				
	A	B	X	C	D	A	B	X	C	D
0.1	277	263	–244	112	–231	–31549	–20511	–2548	–762	15226
0.2	192	34	–427	–274	–731	–26272	–19379	–4726	–2456	8792
0.3	139	–150	–548	–563	–1099	–21898	–16651	–6554	–4531	3940
0.4	111	–274	–603	–756	–1334	–18232	–14235	–8053	–5782	502
0.5	99	–342	–589	–854	–1438	–15073	–12019	–9246	–6281	–1694
0.6	95	–359	–503	–860	–1410	–12226	–9890	–10152	–6099	–2818
0.7	91	–328	–341	–776	–1252	–9493	–7735	–10793	–5308	–3039
0.8	79	–255	–101	–603	–964	–6676	–5444	–11190	–3980	–2530
0.9	52	–144	221	–344	–547	–3577	–2903	–11363	–2187	–1460

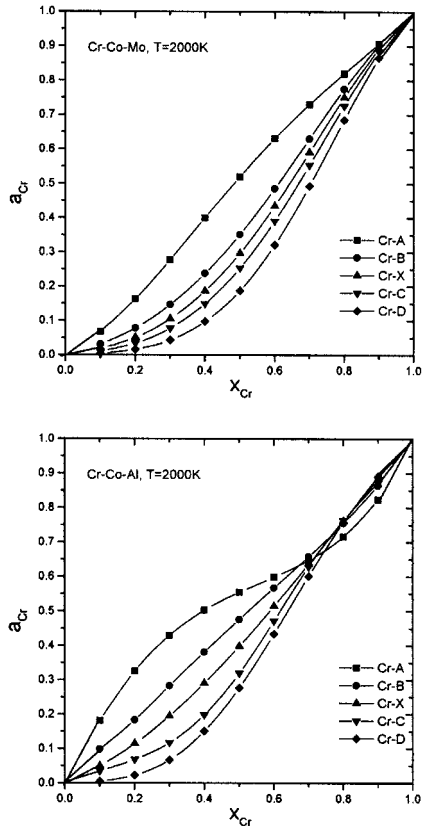

Fig. 3. The dependence of the chromium activity on composition for both the investigated systems at 2000 K.

TABLE V. Partial molar Gibbs energies for chromium, G_{Cr}^{xs} and G_{Cr}^{M} (in J/mol), activity coefficients and activities for chromium in the systems Cr-Co-Mo (a) and Cr-Co-Al (b) at the temperature of 2000 K

– (a): Cr–Co–Mo

x_{Cr}	Section	$G^{xs}{}_{Cr}$	γCr	aCr	G_{Cr}^{M}
0.9		-655.088	0.674377	0.067438	-44838.3
0.8		-346.216	0.812034	0.162407	-30223.9
0.7		-133.856	0.922655	0.276796	-21358.2
0.6		-1.93951	0.998834	0.399534	-15255.5
0.5	Cr - A	65.6	1.04024	0.52012	-10869.7
0.4		84.83	1.05234	0.631404	-7645.71
0.3		71.81775	1.044137	0.730896	-5212.61
0.2		42.6305	1.025969	0.820775	-3284.13
0.1		13.3355	1.008052	0.907247	-1618.58
0.1		-1985.51	0.302984	0.030298	-58142.5
0.2		-1562.77	0.390689	0.078138	-42389.4
0.3		-1196	0.487109	0.146133	-31979.6
0.4		-869.149	0.592916	0.237167	-23927.6
0.5	Cr - B	-586.755	0.702668	0.351334	-17393.2
0.6		-353.34	0.808563	0.485138	-12027.4
0.7		-173.43	0.900955	0.630668	-7665.09
0.8		-51.5527	0.969472	0.775578	-4225.96
0.9		7.766136	1.004681	0.904213	-1674.27
0.9		-10.3181	0.993814	0.894433	-1855.12
0.8		-105.482	0.938534	0.750827	-4765.25
0.7		-282.345	0.843833	0.590683	-8754.24
0.6		-537.759	0.72368	0.434208	-13871.6
0.5	Cr - X	-868.576	0.593121	0.29656	-20211.4
0.4		-1271.65	0.465444	0.186178	-27952.6
0.3		-1743.83	0.350382	0.105115	-37458
0.2		-2281.97	0.253506	0.050701	-49581.5
0.1		-2882.93	0.176616	0.017662	-67116.7
0.1		-3712.74	0.107225	0.010722	-75414.8
0.2		-2934.95	0.171176	0.034235	-56111.2
0.3		-2245.38	0.259146	0.077744	-42473.5
0.4		-1643.98	0.372067	0.148827	-31675.9
0.5	Cr - C	-1132.75	0.505993	0.252996	-22853.2
0.6		-713.73	0.651008	0.390605	-15631.3
0.7		-388.924	0.791443	0.55401	-9820.03
0.8		-160.355	0.908067	0.726454	-5313.98
0.9		-30.0408	0.982096	0.883886	-2052.34
0.1		-5301.76	0.041236	0.004124	-91305
0.2		-4189.71	0.080486	0.016097	-68658.8
0.3		-3207.21	0.145322	0.043597	-52091.8
0.4		-2354.78	0.242646	0.097058	-38783.8
0.5	Cr - D	-1632.91	0.374552	0.187276	-27854.8
0.6		-1042.13	0.534336	0.320602	-18915.3
0.7		-582.935	0.704283	0.492998	-11760.1
0.8		-255.843	0.857389	0.685912	-6268.86
0.9		-61.3618	0.96377	0.867393	-2365.55

TABLE V. Contd.

– (a): Cr–Co–Mo

x_{Cr}	Section	$G^{xs}{}_{Cr}$	γCr	aCr	$G_{Cr}{}^{M}$
0.9		9877.94	1.811318	0.181132	-28409.4
0.8		8062.311	1.623953	0.324791	-18699.4
0.7		5965.302	1.431539	0.429462	-14054.4
0.6		3784.44	1.255576	0.50223	-11451.6
0.5	Cr - A	1717.256	1.108796	0.554398	-9808.4
0.4		-38.7229	0.997674	0.598604	-8532.73
0.3		-1285.97	0.925577	0.647904	-7216.76
0.2		-1826.95	0.895949	0.716759	-5537.38
0.1		-1464.13	0.915713	0.824142	-3216.07
0.1		-348.938	0.979234	0.097923	-38636.3
0.2		-1457.08	0.916102	0.18322	-28218.8
0.3		-969.706	0.94335	0.283005	-20989.4
0.4		-794.064	0.953368	0.381347	-16030.1
0.5	Cr - B	-817.893	0.952002	0.476001	-12343.5
0.6		-928.933	0.945666	0.5674	-9422.94
0.7		-1014.92	0.940788	0.658552	-6945.72
0.8		-963.606	0.943696	0.754957	-4674.04
0.9		-662.718	0.960928	0.864835	-2414.65
0.9		-316.039	0.981173	0.883056	-2067.97
0.8		-833.98	0.951082	0.760865	-4544.41
0.7		-1574.91	0.909633	0.636743	-7505.7
0.6		-2559.91	0.857313	0.514388	-11053.9
0.5	Cr - X	-3810.08	0.79522	0.39761	-15335.7
0.4		-5346.5	0.725035	0.290014	-20582.6
0.3		-7190.25	0.648938	0.194681	-27209.9
0.2		-9362.43	0.569468	0.113894	-36124.2
0.1		-11884.1	0.489336	0.048934	-50171.5
0.1		-17452.7	0.350079	0.035008	-55740.1
0.2		-17784.5	0.343163	0.068633	-44546.2
0.3		-15618.8	0.390899	0.11727	-35638.4
0.4		-11681.4	0.495338	0.198135	-26917.5
0.5	Cr - C	-7475.26	0.63791	0.318955	-19000.9
0.6		-4002.96	0.786049	0.471629	-12497
0.7		-1767.03	0.899183	0.629428	-7697.82
0.8		-769.815	0.954759	0.763807	-4480.25
0.9		-513.472	0.969592	0.872633	-2265.41
0.1		-50332.4	0.048462	0.004846	-88619.8
0.2		-36130.7	0.113849	0.02277	-62892.4
0.3		-24877.1	0.224003	0.067201	-44896.8
0.4		-16230.6	0.376777	0.150711	-31466.7
0.5	Cr - D	-9850.11	0.553009	0.276505	-21375.8
0.6		-5394.54	0.722943	0.433766	-13888.5
0.7		-2522.81	0.859228	0.60146	-8453.61
0.8		-893.868	0.947663	0.75813	-4604.3
0.9		-166.621	0.99003	0.891027	-1918.56

CONCLUSIONS

Based on the obtained results, the following can be concluded:

— For Cr–Co–Mo system:

The integral molar Gibbs excess energies for this ternary system have negative values in the greatest part of the system – only in section A and alloys with low chromium content (less then 0.2) in the sections B and X are positive values obtained. This means that the components in the investigated system are well miscible, except in the part of the system nearer to the chromium–molybdenium side. This can also be seen from the chromium activity curves. As can be seen from Fig. 3, the chromium activities for all investigated sections show a negative deviation from the ideal behaviour, except for section A, where a slight positive deviation is noticed. This points to the fact that the chromium behaves like a solvent for the other two components, which is also shown by the values of the chromium activity, which are less then unity in the greatest part of the system.

— For Cr–Co–Al system:

The integral molar Gibbs excess energies for this ternary system also have negative values in the greatest part of the system – only alloys with a chromium molar content less then 0.5 in the section D have positive values. As for the chromium activity curves, the only positive deviation from the ideal solution law can be noticed for the alloys with a chromium molar content less then 0.5 in the section A, while all the other sections show a negative tendency. This fact indicates that this system has a similar thermodynamic behaviour to the previous one.

The obtained results for the thermodynamic properties in the ternary systems Cr–Co–Mo and Cr–Co–Al are a contribution to the better understanding of the thermodynamic behaviour of these alloys, which is very important in the present day wide field of material designing.

И З В О Д

ОДРЕЂИВАЊЕ ТЕРМОДИНАМИЧКИХ КАРАКТЕРИССТИКА СИСТЕМА Cr–Co–Me (Me = Mo, Al) ПРЕДВИЂАЊЕМ ПО ОПШТЕМ МОДЕЛУ РАСТВОРА

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Резултати одређивања термодинамичких карактеристика тернарних система Cr–Co–Me (Me = Mo, Al) предвиђањем по општем моделу раствора, представљени су у овом раду. За пет пресека (са молским односом: Co : Me = 2:8, 4:6, 5:5, 6:4, 8:2) испитиваних у оба тернарна система на температури 2000 K, прорачунате су вредности интегралних моларних Гибсових енергија вишка, као и активности, коефицијенти активности и парцијалне моларне Гибсове енергије за хром.

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