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Preparation of High Purity Metals by Crystallization Methods

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Abstract. This paper presents limit values of equilibrium distribution coefficients of admixtures in basic metals and the periodical correlation dependences of the distribution coefficients. For high melting-point metals activation neutron analysis, X-ray topography and SSMS were applied to establish effective distribution coefficients of selected admixtures in metals as well as the structural perfection of single crystals.

1. INTRODUCTION

High purity metals with high or medium melting temperature are nowadays remelted in arc, plasma, ion, electron beam and other furnaces. The refining effects of these melting methods are controlled by crystallization processes on the crystal-melt boundary (normal freezing, zone melting, Czochralski method, etc).

Calculation of the solidus and liquidus curves in binary system A-B, was worked out by Kuchar [1]. These curves are - especially in the region adjacent to the essential component - expressed in the form of polynomials of the second grade [2-5]. The equilibrium state is controlled by thermodynamical regularities.

2. DISTRIBUTION COEFFICIENT

The distribution coefficient is defined as an isothermal ratio of admixture concentration on the solidus curve X_S and on the liquidus curve X_L in binary element-admixture system $k_0 = X_S / X_L$ respectively, as its limit value $k_0 \lim$ for $X \rightarrow 0$. The equilibrium distribution coefficient takes the values $k_0 > 1$ for systems, in which the admixture causes a temperature rise of the basic component, and the values $k_0 < 1$ for those admixtures causing a temperature drop of the basic component.

Equilibrium distribution coefficients characterize the behaviour and segregation of admixtures during crystallization at the solidus-liquidus interface, refining processes, preparation of single crystals and the study of inhomogeneities in real alloys. Some gave us reliable information about the distributing ability of individual admixture elements in the basic matter in crystallization processes during which the admixture with $k_0 > 1$ are enriched on the axes of crystallizing dendrites, and vice versa, the admixtures with $k_0 < 1$ are enriched in interdendritic spaces and in the finally solidifying mother melts during the dendritic segregation which always accompanies solidification of substances in reality. In selective refining metallurgical crystallization processes used to prepare high purity metals (as well as substances and metal single crystals, such as zone melting or normal freezing with the material removal) an effective distribution of admixtures in their successive accumulation occurs, so that admixtures with $k_0 > 1$ accumulate at the beginning and admixtures with $k_0 < 1$ at the end of the refined ingot. A knowledge of distribution coefficient values is important for prediction of the refining efficiency in view of the fact that the purity can be influenced [6-12].

Our paper presents a systematic study of the solidus and liquidus curves of available binary systems for these 50 basic elements and 3 compounds:

- Iron Fe
- Non-ferrous metals Co, Ni, Cu, Ga, Cd, In, Sn, Sb, Pb, Te
- Light metals Al
- Noble metals Ag, Au, Ru, Rh, Pd, Os, Ir, Pt
- Refractory metals Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Re
- Lanthanoids La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Sc, Y
- Radioactive metals U, Th, Pu

Table 1. Distribution coefficients of admixtures in Al, Ti, Fe, Ni, Cu, Nb, Mo, Ag, La, U

Element	Al	Ti	Fe	Ni	Cu	Nb	Mo	Ag	La	U
1 H	<0.1		~0.3		0.6				1.15	0.80
2 He	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
3 Li	0.58				0.45			0.50	>1	<0.1
4 Be	0.30	0.12	0.82	0.36	0.34		0.041	0.32		0.34
5 B	0.26		0.046	0.0062	0.057	0.041	0.12			<0.1
6 C		0.37	0.13	0.22	~0.1	0.62	0.065		0.36	0.20
7 N	<0.1					~0.8			>1	<0.1
8 O		1.65	0.13	0.016	0.023	0.22		~0.01	>1	0.088
9 F										
10 Ne	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
11 Na	0.018					~0.01			>1	
12 Mg	0.30		0.17	0.16	0.11	0.050		0.56	0.60	<0.1
13 Al	1.00	1.37	0.87	0.87	0.95	0.45	0.44	0.49	<0.1	0.57
14 Si	0.10	0.36	0.64	0.36	0.43	0.16	0.19	<0.1		0.14
15 P	<0.1	0.033	0.13	0.0061	0.11			<0.1		
16 S	<0.01	0.00081	0.055	0.0015	~0.01			~0.01	<0.1	<0.1
17 Cl									<0.1	
18 Ar	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
20 Ca	0.055			<0.1	0.05			<0.1	0.62	
21 Sc	<1	0.38	0.057	0.046	~0.1	<0.1	~0.1	0.45	0.88	
22 Ti	9.40	1.00	0.34	0.73	0.35	0.59	0.74	~1	<1	~1.5
23 V	5.80	0.74	0.82	0.97	>1	0.85	0.75	~1	0.24	0.56
24 Cr	1.84	0.60	0.90	0.82	0.54	0.82	0.71	~1	<0.1	0.17
25 Mn	0.76	0.31	0.68	0.72	0.37		~0.2	>1	0.038	0.17
26 Fe	0.023	0.26	1.00	0.94	1.32	0.20	0.48	>1	0.032	0.099
27 Co	0.024	0.20	0.85	1.03	1.53	0.054	0.29	>1	<0.1	0.054
28 Ni	0.0071	0.19	0.69	1.00	1.68	0.055	0.15	>1	<0.1	0.029
29 Cu	0.14	0.19	0.80	0.82	1.00	0.022		0.51	<0.1	<0.1
30 Zn	0.43		0.77	0.61	0.72			0.38	<0.1	<0.1
31 Ga	0.088	0.73	0.76	0.63	0.59	0.33	~0.1	0.36	0.32	<0.1
32 Ge	0.080	0.74	0.77	0.52	0.40	0.21	0.15	0.23	<0.1	0.26
33 As	<0.1	0.074	0.20	0.084	0.19			0.16		
34 Se	<0.01									
36 Kr	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
38 Sr	<0.1			<0.1	~0.025			<0.1		
39 Y	0.028	0.10	0.054	0.053	0.056		~0.05	0.17	1.60	
40 Zr	2.24	0.75	0.035	0.086	0.02	0.57	0.26	<1		1.92
41 Nb	4.18	1.23	0.22	0.51	1.90	1.00	0.80		1.28	2.27
42 Mo	2.47	1.71	0.72	0.89	~3	0.73	1.00		>1	1.34
43 Tc	<1		1.03	1.13	>1					
44 Ru	<1	0.53	1.03	1.20	>1	0.47	0.60	>1		0.23
45 Rh	<0.1	0.32	0.76	1.30	2.13	0.35	0.34	>1	<1	0.20
46 Pd	<0.1	0.33	0.47	0.52	1.09	0.54	0.21	1.94		0.32
47 Ag	0.34	0.68		0.80	0.30			1.00	0.22	
48 Cd	0.053			<0.1	0.64			0.73	0.43	<0.1
49 In	0.010		0.20	0.24	0.23			0.57	0.41	
50 Sn	0.0078	0.89	0.27	0.23	0.16	0.43		0.50	<0.1	<0.1
51 Sb	0.042	0.38	0.13	0.23	0.17	0.23		0.21	<0.1	<0.1
52 Te	<0.01				0.001			<0.01	<0.1	
54 Xe	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
57 La	0.0032	0.42	0.044	<0.1	~0.06	0.057	~0.07	0.0033	1.00	
58 Ce	0.0035	0.20	0.015	0.002	0.024	0.20		0.052	0.90	0.13
59 Pr	0.0031			<0.1	~0.08			0.0036	1.04	
60 Nd	0.003	0.24	~0.11		~0.07			0.018	1.10	
62 Sm	<0.1		0.0062		0.094	0.18		0.035	1.52	
64 Gd		0.12	0.065	0.082			0.072	0.055	1.59	
65 Tb	0.018							0.080	>1	
66 Dy	<0.1							0.084		
67 Ho	<0.1		<0.1		<0.1			0.090		
68 Er	<0.1	0.093	0.083	<0.1				0.239	<0.1	
69 Tm	0.0081		<0.1					0.22		
70 Yb	<0.1							0.12		
71 Lu			<0.1					0.29		
72 Hf	4.44	0.93	0.21	0.16	~0.6	0.79	0.58	<1		1.98
73 Ta	>1	2.17	0.32	0.74	>2	1.27	1.05		<0.1	4.42
74 W	>1	3.60	0.85	0.67	>2	1.21	1.45			1.28
75 Re	>1	1.62	1.22	1.96	>1	0.97	0.86			0.83
76 Os		0.72	1.11	>1	>1	0.65	0.69	>1		0.50
77 Ir		0.57	1.05	>1	2.38	0.41	0.37	>1	<0.1	0.24
78 Pt	0.44	0.31	0.60	1.032	1.72	0.055	0.24	2.45		0.28
79 Au	0.069	0.36	0.39	0.35	0.50	0.43		1.20	<0.1	0.55
80 Hg	0.12			~0.1	~0.2			0.50		<0.1
81 Tl	<0.1			0.24	0.072			0.20	0.36	
82 Pb	0.072	0.38		0.075	0.01			0.25	<0.1	<0.1
83 Bi	0.039	0.36		<0.1	0.001			0.058	0.28	
86 Rn	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
90 Th	0.050		<0.1	0.002	0.084		~0.1	~0.01	1.20	<0.1
92 U	0.0046	0.80	<0.1	0.034	~0.025	0.49	0.29	~0.05		1.00
93 Np										0.68
94 Pu	0.0037	0.27	<0.1	0.093	~0.01		~0.15		0.70	0.54

Figure 1: Periodical dependence of distribution coefficients of admixtures in Fe on atomic number

Figure 2: Periodical dependence of distribution coefficients of admixtures in Ni on atomic number

Figure 3: Periodical dependence of distribution coefficients of admixtures in Nb on atomic number

• Semiconductors Si, Ge, and compounds GaAs, GaSb, CdTe

Table 1 presents the values of the equilibrium distribution coefficients of admixtures in 10 basic elements (Al, Ti, Fe, Ni, Cu, Nb, Mo, Ag, La, U) obtained from the existing binary alloy phase diagrams as well as from experimentally obtained concentration admixture gradients for which the authors used various melting techniques, such as refining by zone melting or directional crystallization.

3. PERIODICITY OF DISTRIBUTION COEFFICIENTS

The values of distribution coefficients may be objectively graphically arranged into a periodical correlation dependence on the atomic number of admixture (fig. 1, 2, 3). Similar periodical dependences were proven by the authors [1,6,9,11] for more than 50 elements of the periodical system [13-16]. These correlation dependences yield a certain periodicity of values k_0 in individual periods mutually divided by the value of inert gases -He, -Ne, -Ar, -Kr, -Xe, -Rn (minima of correlation curves). The maxima of correlation curves are seen in each period.

The values of k_0 and correlative relations shown make it possible [6]:

- to determine the unknown k_0 values and to predict the behaviour of admixtures during crystallization processes
- to estimate the practical realization of zone melting or directional crystallization of various basic substances, to choose suitable materials for those processes, and to predict the refining grade
- to achieve objective control of crystallization processes in refining metallurgy
- to achieve controlled microalloying and doping of admixtures when cultivating single crystals as well as technical alloys in which they increase a number of physical metallurgical properties
- to calculate constitutional undercooling in solidifying materials in the crystal-melt boundary
- to predict the basic types of binary diagrams
- to predict the distribution ability and enriching of foreign admixtures with $k_0 > 1$ on the dendritus axis and the accumulation of admixtures with $k_0 < 1$ in interdendritic spaces in the mother melt during the dendritic segregation which always accompanies the solidification of substances
- to calculate the melting temperature decrease or increase of the basic component at the given admixture concentration
- to determine the range of the crystallization interval with respect to the control of the production processes of technical alloys by classic or continuous casting and solidification of substances.

4. EXPERIMENTAL

Zone melting and directional crystallization is one of the most effective methods for the preparation of high purity materials. Controlled crystallization is employed for the preparation of oriented single crystals. During zone melting the process of redistribution of impurities occurs at the crystal-melt interface.

Figure 4: Effective distribution coefficients of W, Ta and Ir in niobium.

We prepared single crystals of high melting-point metals (W, Mo, Ta, Nb, V, Re) and their alloys (Nb-Zr, W-Mo, Mo-W, W-Re...) by the method of electron beam zone melting with "floating zone" in our department. The stability of the remelted zone depends on the surface tension, density of the melt, concentration of admixtures and the direction of zone movement. The maximum diameters of single crystal rods, which are prepared using the above-mentioned method, are for molybdenum and niobium 12 mm, for tantalum 10 mm and for tungsten 6 mm. The length of the single crystal part is 200 mm. We are able to produce single crystals with defined high purity, orientation and structural perfection [17].

Distribution of selected impurities was experimentally performed with nucleides as the indicators during zone melting of metals [18-21]. For high melting-point metals activation neutron analysis was applied to establish effective distribution coefficients in selected admixtures in metals [22].

Effective distribution coefficients Ir, Ta and W in niobium were determined for three different zoning speeds - see fig. 4. Iridium was alloyed into niobium at a concentration of 250 wt ppm. The equilibrium distribution coefficients of Ir, Ta and W in niobium were calculated from these values: $k_0 = 0.415$ for Ir, which is in good agreement with the theoretical value $k_{0 \text{ lim}} = 0.409$, $k_0 = 1.23$ for Ta, and $k_0 = 1.61$ for W in niobium. All these experimental values confirmed the periodical dependence of the distribution coefficient values of the admixture on its atomic number [1].

Characteristic macro- and microsegregations in a dependence on the concentration of admixtures and on the molten zone length were found during preparation of molybdenum single crystals alloyed by iridium, which may be imputed to the convection in the molten zone [23]. In Molybdenum single crystals alloyed by iridium at contents between 0,01 - 1,5 at.% Ir, micro-inhomogeneities such as crystal cores, striations and cellular structure arise, depending on the crystallization conditions. Dislocation substructure is affected by radial inhomogeneities of the growth cores much more conspicuously than by axial striations or cellular substructure.

Critical concentration $C^* = 0.2$ at.% Ir was found for the zone length 4 mm, when the plane surface crystal-melt loses its stability - fig. 5. Iridium is concentrated in the central part of the rod. Developed cellular structure with low dislocation density was observed for concentrations of Ir in molybdenum over 0.4 at.% (fig. 5).

Figure 5: Dependence of dislocation density on concentration of Ir in molybdenum single crystals.

The investigation established that:

- Zone length (volume of melt) defines the main type of convection - hydrostatic or Marangoni's convections. There are micro-inhomogeneities in the crystal in the form of growth wets or growth cores arising in cases where the critical zone length is exceeded.
- The crystal structure is influenced by the concentration of admixtures and their distribution in a radial direction.
- Cellular-fibral structure attains a high degree of structure perfection at defined concentrations of alloyed elements.

- d) Concentration gradients of B-striations influence crystal perfection over the critical concentration of Ir. An inhomogenous structure with a high density of dislocations is created in peripheral areas of crystals.
- e) B-cores can be largely eliminated by the use of stimulated convection (rotation, external magnetic field, etc).

A plasma furnace [24], which was developed at the Dept. of Nonferrous Metals TU Ostrava, effects remelting of pure metals with middle and high melting temperature in an inert gaseous atmosphere. The furnace works with a low-temperature plasma burner and a horizontal copper crystallizer with water cooling. It makes it possible to remelt and refine metals (Fe, Co, Ni, Ti...), special highly alloyed alloys (Fe-Si, Fe-Ni, Fe-Cr, Fe-Al-Mo, V-N...) and intermetallic compounds (NiTi, Ni₃Al, Ti₃Al...) [25,26].

5. CONCLUSION

Theoretical and experimental results have found a wide variety of applications in various branches of research as well as in practical crystallization and refining processes, by which the significance of the values, not only for metallurgy but also for other new branches of technology, is confirmed.

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