EQUILIBRIUM DISTRIBUTION COEFFICIENTS OF ADMIXTURES IN REFRACTORY METALS

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ROVNOVÁŽNÉ ROZDĚLOVACÍ KOEFICIENTY PŘÍMĚSÍ VE VYSOKOTAVITELNÝCH KOVECH

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Abstrakt

Během rafinačních krystalizačních procesů dochází na fázovém rozhraní k přerozdělování příměsí a nečistot. Základní charakteristikou rozdělovaní příměsí a nečistot mezi tuhou a tekutou fází je rovnovážný rozdělovací koeficient k_0. Jeho znalost je důležitá pro zvolení vhodné krystalizační metody rafinace, přípravu monokrystalů a studium segregačních mikro- a makronehomogenit. Rovnovážný rozdělovací koeficient představuje hlavní materiálový parametr pro přípravu vysoce čistých materiálů rafinačními procesy, jako je zonální tavení a směrová krystalizace.

V této práci jsou prezentovány limitní hodnoty rovnovážných rozdělovacích koeficientů pro systémy Cr, Mo, Nb, Re, Ta, V, W - příměs jako výsledek systematického studia křivek solidu a likvidu v těchto binárních systémech. Z hodnot rozdělovacích koeficientů pro systémy V, Nb - příměs byly sestrojeny periodické závislosti rovnovážných rozdělovacích koeficientů příměsí na protonovém čísle příměsi.

Abstract

During refining crystallization processes a distribution of admixtures and impurities at the phase interface occurs. The distribution of admixtures and impurities between solidus and liquidus phases is characterized by equilibrium distribution coefficient. Knowledge of the distribution coefficient is important for the choice of a convenient crystallization method of refining, preparation of single crystals and study of segregation micro- and macroinhomogeneities in real alloys. The equilibrium distribution coefficient represents the main material parameter for the preparation of high pure materials by refining processes as the zone melting and directional crystallization.

In the paper the limit values of the equilibrium distribution coefficients of admixtures in Cr, Mo, Nb, Re, Ta, V, W as a result of the systematic study of solidus and liquidus curves in binary systems basic metals - admixture are presented. The periodical dependencies of the distribution coefficients of admixtures on the admixture atomic number were determined for systems niobium - , vanadium - admixture.

Key words: distribution coefficient, refractory metals, refining, vanadium, niobium

1. Introduction

The processes of zone melting and directional crystallization are used for preparation of high purity metals. In these selected crystallization processes the distribution of admixture (impurity) B in basic substance A occurs at the liquidus and solidus phase boundary of the materials. The distribution results from the different concentration admixture (impurity) in the liquidus and solidus phase at the thermodynamic equilibrium. The concentration conditions can be determined by means of the corresponding equilibrium binary diagrams.

2. Distribution coefficient

The equilibrium distribution coefficient is defined as an isothermal ratio of admixture concentrations on the solidus curve X_{SB} and the liquidus curve X_{LB} in binary metal A - admixture B systems (see Fig.1):

(T = const.) (1)

and its limit value being k_{olim} for $X_{S,LB} \rightarrow 0$. This is very important especially in the edge areas of binary diagrams where limited amounts of admixtures occur and in these areas value k_{olim} might be accepted as constant value. The equilibrium distribution coefficient takes the values $k_o>1$ for systems (Fig.1b) in which the admixtures (impurities) cause a temperature rise of the basic component A and the values $k_o<1$ for the admixtures (impurities) causing a temperature decrease of the basic component A (Fig.1a).

The 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. They give us reliable information about the distributing ability of individual admixture elements in the basic matter in crystallization processes during which the admixtures with $k_o>1$ are enriched on the axes of crystallizing dendrites or cells, and vice versa, the admixtures with $k_o<1$ are enriched in interdendritic spaces and in the finally solidifying mother melts during the dendritic or cellular segregation which always accompanies solidification of substance in reality. The knowledge of distribution coefficient values is important for the refining efficiency prediction in the view of the purity influencing.

a) b)

Fig.1 The definition of the equilibrium distribution coefficient

a) The admixture B decreases the melting point of A, b) The admixture B increases the melting point of A

The equilibrium distribution coefficients were reviewed (by the authors) on the base of the new published thermodynamic data (Tab.1) - the melting points T_{MA} and the melting enthalpies ΔH_M of metals - and in consequence of update or representation of new binary diagrams. The specification of the solidus and liquidus curves, the calculation of equations of these curves and the determination of new values of the equilibrium distribution coefficients for the binary systems Cr, Mo, Nb, Re, Ta, V, W - admixture were carried out. The determination of distribution coefficients was necessary for the

mathematical and thermodynamic expression of the solidus and liquidus curves. For that reason, a method [1] was work out by Kuchař. According to this method, the courses of these curves, especially in the region adjacent to the pure basic component, are expressed in the form of the second grade polynomials:

(2)

where T_{MA} is the melting point of the basic element A, $X_{S,LB}$ are the concentrations of B admixture in atomic percent. The curves are thermodynamically controlled (Hayes-Chipman´s thermodynamical formula [2]) and a database of phase data exists for many binary diagrams A-B at the Department of nonferrous metals, refining and recycling VŠB-TU Ostrava. are used Experimental data from binary diagrams A - B by various authors are used for determination of regression coefficients in equations (2) and they can be calculated by the method [1] of last squares of deviations.

Taking into account the temperature or concentration dependence from the course of distribution coefficient it is possible to express the equilibrium distribution coefficient k_0 utilizing the parameters $a_{S,L}$ and $b_{S,L}$ from equation (2) in the following shape:

(3)

By extrapolation of the solidus and liquidus curves courses to the area of diluted solution ($X_{S,LB} \rightarrow 0$), i.e. for X approaching to zero, the limit value of the equilibrium distribution coefficient kolim can be calculated from equation (3):

(4)

which is possible in the limit areas up to about $\pm$ 10K from the melting temperature T_{MA}. The value $k_{0\ lim}$ is the main material parameter which expresses the segregation ability of admixture B in base element A during crystallization.

The parameters $a_{S,L}$ and $b_{S,L}$ from equation (2) for the systems vanadium - admixture (as an example) including the range of their validity from the melting point to a particular defined temperature (°C) are presented in Table 2. The limit values k_{olim} of equilibrium distribution coefficients of admixtures in Cr, Mo, Nb, Re, Ta, V, W are shown in Table 3 in dependence on the increasing atomic number of the admixture. For the systems in which we do not have enough input data or whose binary diagrams do not exist we included approximate predicted values of k_o by symbols <1 or >1. This is valid also for k_o of inert gases He, Ne, Ar, Kr, Xe and Rn (k_o<0,001).

Table 1 The used values of melting points and melting enthalpy for Cr, Mo, Nb, Re, Ta and W [3]

Table 2 Calculated parameters a_S, b_S, a_L, b_L for admixtures in vanadium and the temperature range of validity of equations

Table 3 The limit distribution coefficients of admixtures in Cr, Mo, Nb, Re, Ta, V and W

3. Periodical correlation dependence of equilibrium distribution coefficients of admixtures on atomic number of admixtures

The distribution coefficient characterizes admixture elements distributing when they are used as alloying elements of basic metals. One of the most important correlations of the distribution coefficients is their periodical dependence on the atomic number of admixture.

Two examples of those correlation dependencies are shown in Figs 2 and 3: the dependence of the distribution coefficients of admixtures in niobium (Fig.2) and in vanadium (Fig.3) on the atomic number of the admixtures.

Fig.2 Periodical correlation dependence of equilibrium distribution coefficients of admixtures in niobium on atomic number of admixtures

Fig.3 Periodical correlation dependence of equilibrium distribution coefficients of admixtures in vanadium on atomic number of admixtures

These correlations were determined from the k_o values presented in Table 3. In the above mentioned graphical dependencies the minimums of k_o are the values for inert gases He, Ne, Ar, Kr, Xe and Rn which are practically indissoluble in niobium and vanadium and mutually separate individual periods. For vanadium, in the first three periods (Fig.3) the maximums of ko are formed by the values of k_o of admixtures H, N and Al. The fourth period is doubled and there are two maximums of k_o, the higher one for vanadium but the following elements Cr, Mn, Fe and Co have the distribution coefficient k_o>0,6, which means that these admixtures have low distributing ability in vanadium, and the lower one for gallium. The fifth period is as well doubled and the first higher maximum is formed by Mo, Tc, Ru (k_o>1) and the second lower one by tin. In the sixth period the maximum is formed by W, Re and

Os, these admixtures have the values of distribution coefficients $k_0>1$. For the group of rare-earth metals very little number of binary diagrams is known so far. From the correlation dependence of k_0 on the admixture atomic number we may presume that the k_0 values of other admixtures from the rare-earth metals and actinoids will be less than 0,1.

Similar periodical correlation dependencies of equilibrium distribution coefficients of admixtures on atomic number of admixtures were determined for systems of Cr, Mo, Nb, Re, Ta and W. Only a few binary diagrams have been determined for systems W, Re, Ta - admixture because of their high melting points and more difficult determination of cooling curves by the differential thermal analysis.

Periodical correlation dependencies of the equilibrium distribution coefficients of admixtures in basic metals on atomic number usually allow to:

predict some unknown values of k_0 admixtures and thus their behaviour during crystallization processes (e.g. directional crystallization and zone melting)

inform about the suitability of the zone melting or directional crystallization application for preparation of high purity materials

choose suitable input materials for such refining processes and evaluate an attainable degree of refining

control micro-alloying and dotting by admixtures during crystal growing even from technical alloys whose leads to their physical characteristics improvement

calculate concentration undercooling in solidified materials on the boundary crystal - melt and in that way to forecast the growth morphology

forecast basic types of unknown binary diagrams

forecast the distribution ability and enrichment of foreign admixtures with $k_0>1$ in the dendrite axes, accumulation of admixtures with $k_0<1$in interdendritic areas, in the mother melt during dendritic segregation which usually accompanies real solidification. The more k_0 differs from 1, the higher is the efficiency of admixture distributing [4]

calculate the decrease or increase of the melting temperature of the basic element for a given admixture concentration

determine the width of solidification interval [5,6], which is important for casting and solidification of the materials in production processes of technical alloys.

4. CONCLUSIONS

The equilibrium distribution coefficients of various admixtures in the refractory metals Cr, Mo, Nb, Re, Ta, V and W were computed from binary diagrams. The periodic dependencies of equilibrium distribution coefficients of admixtures k_0 on atomic number of the admixture were determined for Nb and V. These dependencies allow to predict the behaviour of admixtures on the crystal - melt interface during crystallization processes even for the admixtures whose binary diagrams are not known yet.

The paper is a contribution to the theory and practice of high purity materials preparation by means of crystallization methods.

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