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A NEW APPROACH TO EVALUATING THE CHEMICAL MICRO-HETEROGENEITY OF A CONTINUOUSLY CAST STEEL SLAB

NOV NAČIN OCENJEVANJA KEMIJSKE MIKROHETEROGENOSTI KONTINUIRNO ULITIH SLABOV

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The paper deals with a new approach to measuring and evaluating the chemical micro-heterogeneity of the elements in solidified poly-component metallic systems. The original approach is based on experimental measurements made on the samples taken from characteristic places in a casting and the subsequent application of an original mathematical model for determining the element-distribution profile, characterizing the most probable distribution of an element concentration in the frame of a dendrite, and an original mathematical model for determining the effective partition coefficients of these elements in the structure of the analyzed alloy. The paper also describes an application of this method in the research of the chemical heterogeneity on a cross-section of a CC steel slab and presents the selected results (indices of the heterogeneity and effective partition coefficients of seven analyzed elements) characterizing the chemical micro-heterogeneity on one-half of the cross-section of this CC steel slab. The following main results were obtained: (*i*) the dendritic heterogeneity of the accompanying elements and impurities is comparatively high; (*ii*) all the analyzed elements segregate during the solidification into an inter-dendritic melt, and their partition coefficient is smaller than one; (*iii*) the effective partition coefficients calculated in this new way inherently include both the effect of segregation in the course of an alloy solidification, and the effect of the homogenization occurring during the solidification as well as during the cooling of an alloy.

Keywords: micro-segregation, effective partition coefficient, continuous casting, steel

Članek obravnava nov način merjenja in ocenjevanja kemijske mikroheterogenosti elementov v večkomponentnih kovinskih sistemih. Izviren način temelji na eksperimentalnih meritvah, narejenih na vzorcih, vzetih iz značilnih mest ulitka, in uporabi izvirnega matematičnega modela za določanje profila razporeditve elementov, kar omogoča oceno najbolj verjetne razporeditve koncentracije elementov v dendrite in določanje efektivnega koeficienta razporeditve teh elementov v strukturi analizirane zlitine. Članek opisuje tudi uporabo te metode pri raziskavi kemijske heterogenosti prečnega prereza kontinuirno ulitega slaba in predstavlja izbrane rezultate (indeks heterogenosti in koeficiente razporeditve sedmih analiziranih elementov) značilne kemijske mikroheterogenosti polovice prereza kontinuirno ulitega slaba. Glavni rezultati so: (*i*) heterogenost spremljajočih elementov in nečistoč je razmeroma velika; (*ii*) vsi analizirani elementi izcejajo med strjevanjem v meddendritno talino, njihov koeficient razporeditve je manjši od ena; (*iii*) na nov način izračunani koeficienti razporeditve vključujejo v sebi oba učinka, to je učinek izcejanja med potekom strjevanja in učinek homogenizacije, ki se pojavi med strjevanjem, in nadaljnjim ohlajanjem zlitine.

Ključne besede: mikroizcejanje, koeficient porazdelitve, kontinuirno ulivanje, jeklo

1 INTRODUCTION

The structure of metallic alloys is one of the factors, which significantly influence their physical and mechanical properties. The formation of a structure is strongly affected by production technology, casting and solidification of these alloys. Chemical heterogeneities are a common problem in castings and solidification processes. A solute segregation either on the macro- or micro-scale is sometimes the cause of unacceptable products due to poor mechanical properties of the resulting non-equilibrium phases.

Micro-segregation refers to a composition variation within a dendritic solidification structure, which has a length scale of the order of only a few micrometers. It is usual to characterize the extent of micro-segregation using a ranking scheme of randomly sampled electron micro-analysis data.[1–4] Thermodynamic quantities are often calculated from the measurements of an as-cast segregation profile, in particular, the partition coefficient. A well-founded technique is thus imperative for evaluating the compositional data from an X-ray microanalysis.[5,6]

Micro-segregation is caused by the redistribution of a solute during the solidification, as a solute is generally injected into the liquid. Its fundamental cause is the difference between the thermodynamic equilibrium solubility of the alloy elements in different phases that coexist in the mushy region during the solidification. This is combined with the inability of the solid-state diffusion to fully return the composition to its equilibrium constant level after the solidification is complete, due to the short times and small diffusion coefficients involved.[7]

A micro-structure prediction is a very difficult task requiring computationally intensive modeling methods, such as the phase field[8] and cellular automata.[9]

The presented paper describes a simple methodology for determining the chemical heterogeneity in metallic poly-component systems, which was developed on the basis of a long-term investigation and mathematical modeling of the segregation processes during the crystallization of metallic alloys at the authors' workplaces.

An original approach to determining the chemical heterogeneity in the structure of a poly-component system is based on the experimental measurements made on the samples taken from characteristic places of the casting. In the selected sections of these samples the concentration of solutes is determined in regular steps. The length of a measured line depends on the dendrite-arm spacing. The line segment, along which the concentration of the elements is measured, should appropriately intersect a number of these dendritic arms (at least five and even more). Depending on the chemical heterogeneity and the structure of the casting the selected sections usually have the lengths of 500 μm to 1000 μm, and the total number of steps, in which the concentration is determined, is set to 101. The method of the quantitative-energy dispersion (ED) or wave dispersion (WD) X-ray spectral micro-analysis is used for determining the concentration of the elements.

After the termination correspondence of the measured concentrations of the elements and the structure of the given alloy is documented, the average dendrite-arm spacing is metallographically determined within the frame of the measured section.

Further procedure is based on statistical processing of the concentration-data sets and the application of the original mathematical model for determining distribution curves of the dendritic segregation of the elements, characterizing the most probable element-concentration distribution in the frame of a dendrite,[10] and the original mathematical model for determining the effective partition coefficients of these elements in the analyzed alloy.

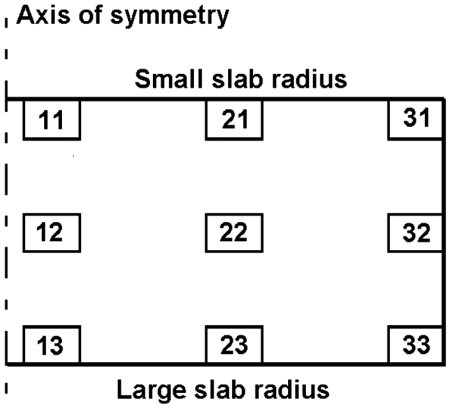

Figure 1: Scheme of a sampling from a slab and marking of the samples
Slika 1: Načrt vzorčenja in oznake vzorcev iz slaba

2 EXPERIMENTAL WORK

A continuously cast steel slab (CC steel slab) with the cross-section dimensions of 1530 mm × 250 mm was chosen for the presentation of the results. The chemical composition of the steel (in mass fractions, *w*/%) was the following: 0.14C; 0.75Mn; 0.23Si; 0.016P; 0.010S; 0.10Cr; 0.050Cu; 0.033Al_{total}.

After the solidification and cooling of the cast slab, a transversal band was cut out, which was then axially divided into halves. Nine samples were taken from one half for determining the chemical heterogeneity as seen on **Figure 1**. The samples had a form of a cube with an edge of about 20 mm, with recorded orientation of its original position in the CC slab.

All samples were prepared with the standard metallographic techniques. On each sample a concentration of seven elements (Al, Si, P, S, Ti, Cr and Mn) were measured along the line of 1000 μm. The distance between the measured points was 10 μm. An analytical, complex JEOL JXA 8600/KEVEX Delta V Sesame and an ED micro-analysis were used for determining the concentration distribution of the elements. As an example, **Figure 2** presents the basic concentration spectra of Mn and Si.

3 RESULTS AND DISCUSSION

The chemical micro-heterogeneity, i.e., the segregation of individual elements at the distances, the order of which is comparable to the dendrite-arm spacing, can be quantitatively evaluated from the basic statistical parameters of the measured concentrations of the elements in individual samples: C_{av} average concentration of an element in the measured section, σ_C standard deviation of the measured concentration of the element, C_{min} minimum and C_{max} maximum concentrations of the element in the same measured section of the sample.

Moreover, it is possible to calculate, from these data, the indices of dendritic heterogeneity I_H of the elements in the measured section as the ratio between the standard

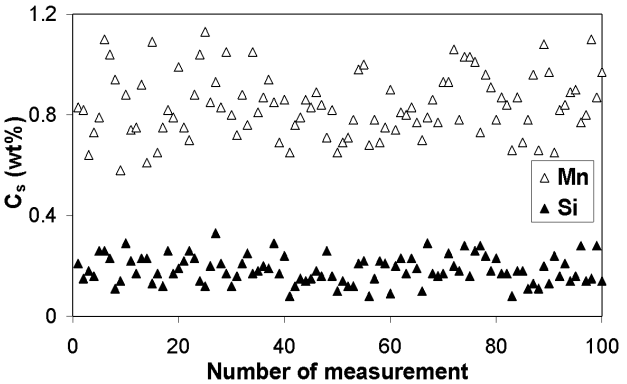

Figure 2: Basic concentration spectra of Mn and Si (sample 21)
Slika 2: Spekter osnovnih koncentracij Mn in Si (vzorec 21)

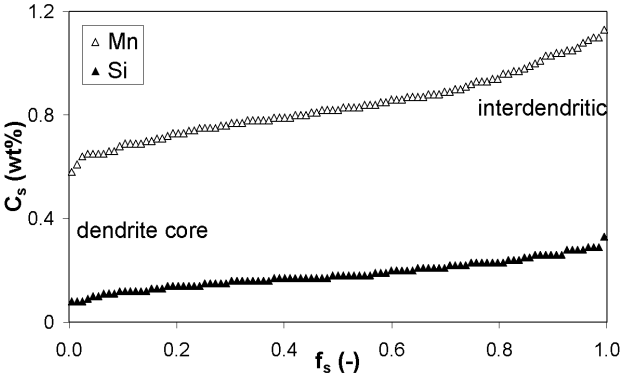

Figure 3: Distribution profiles of Mn and Si constructed from the experimentally obtained data according to the Gungor's method[11] (sample 21)

Slika 3: Profil razporeditve Mn in Si, dobljen iz eksperimentalno izmerjenih podatkov skladno z Gungorjevo metodo[11] (vzorec 21)

deviation σ_C and the average concentration C_{av} of an element.

Then the element-distribution profiles can be plotted according to the Gungor's method[11] from the concentration-data sets measured along the line segment with the length of 1000 μm. The data plotted as the measured weight-percent composition versus the number of data (**Figure 2**) were put in an ascending or descending order and the *x*-axis was converted to the fraction solid (f_S) by dividing each measured data number by the total measured data number. The element composition versus the fraction solid, i.e., the element-distribution profile (the distribution curve of a dendritic segregation) was then plotted; **Figure 3** represents such dependences for manganese and silicon. The slope of such a curve (ascending or descending) depended on whether the element in question enriched the dendrite core or the inter-dendritic area in the course of the solidification.

From these statistical data it is also possible to determine the values of effective partition coefficients k_{ef} for each element analyzed on each sample. The original mathematical model for an effective-partition-coefficient calculation will be outlined here as follows:

The sequence of the arranged concentrations (**Figure 3**) was seen as a distribution of concentrations of a measured element in the direction from the axis ($f_S = 0$) to the boundary ($f_S = 1$) of an average dendrite. The effective partition coefficient k_{ef} was, in this case, defined with the relation:

$$k_{ef}\,(f_S) = C_S\,(f_S)/C_L\,(f_S) \qquad (1)$$

where C_S is the solute concentration in the solid and C_L is its concentration in the melt and the argument (f_S) expresses the dependence of both concentrations on the fraction solid.

A perfect mixing of an element in an interdendritic melt was then assumed (this assumption is the same as, e.g., in the Scheil[12] and Brody-Flemings[1] model of solidification). It was therefore possible to substitute the equation (1) with the following formula:

$$k_{ef}\,(i) = C_i/C_R\,(i) \qquad (2)$$

where C_i is the concentration in the i-th point of a sequence (i.e., in the i-th point of the curve in **Figure 3**) and $C_R(i)$ is the average concentration of the element i in the residual part of the curve (i.e., for $f_S \in \langle i, 1\rangle$), expressed by the relation:

$$C_R(i) = \left(\frac{1}{n-i+1}\right)\cdot\sum_{j=i}^{n} C_j \qquad (3)$$

where n was the number of the measured points. In this way it was possible to determine the values of effective partition coefficients for all $i \in \langle 1, n\rangle$, i.e., for the entire curve characterizing the segregation during the solidification. The effective partition coefficients of all the analyzed elements were calculated with this original method. The average values for the determined effective partition coefficients are listed in **Table 1**. No segregation occurs when $k_{ef} = 1$; the higher the deviation from the number 1 is, the higher is the segregation ability.

The data presented in **Tables 1** and **2** make it possible to evaluate the dendritic heterogeneity (micro-heterogeneity) of the elements in individual samples, and also in the frame of the whole analyzed half of the slab's cross-section. It is obvious that the dendritic heterogeneity of the elements is comparatively high. This is demonstrated with the index of dendritic heterogeneity I_H. It follows from Table 1 that distinct differences exist between micro-heterogeneities of individual elements. The average value of this coefficient for all the analyzed elements and the whole set of nine samples is given in

Table 1: Average values of the heterogeneity index I_H and the effective partition coefficient k_{ef} of the elements in individual samples

Tabela 1: Povprečna vrednost indeksa heterogenosti I_H in koeficienta porazdelitve k_{ef} elementov v posameznem vzorcu

Sample		Element						
		Al	Si	P	S	Ti	Cr	Mn
11	I_H	1.24	0.28	1.22	1.45	0.30	0.22	0.14
	k_{ef}	0.32	0.78	0.33	0.26	0.76	0.83	0.88
12	I_H	1.54	0.30	1.12	1.74	0.29	0.27	0.15
	k_{ef}	0.24	0.77	0.36	0.20	0.78	0.79	0.88
13	I_H	1.44	0.30	1.25	1.48	0.30	0.29	0.15
	k_{ef}	0.27	0.78	0.32	0.26	0.77	0.78	0.88
21	I_H	1.33	0.29	1.58	1.49	0.31	0.24	0.13
	k_{ef}	0.29	0.78	0.24	0.25	0.76	0.81	0.89
22	I_H	1.14	0.28	1.31	1.41	0.30	0.26	0.14
	k_{ef}	0.35	0.78	0.30	0.27	0.77	0.80	0.88
23	I_H	1.56	0.29	1.34	1.86	0.26	0.28	0.13
	k_{ef}	0.24	0.78	0.29	0.18	0.80	0.78	0.89
31	I_H	1.11	0.28	1.22	2.34	0.31	0.23	0.16
	k_{ef}	0.37	0.78	0.33	0.18	0.76	0.82	0.87
32	I_H	1.44	0.27	1.16	1.49	0.34	0.25	0.14
	k_{ef}	0.27	0.79	0.34	0.25	0.74	0.80	0.88
33	I_H	1.32	0.29	1.24	1.64	0.35	0.26	0.13
	k_{ef}	0.30	0.78	0.32	0.22	0.74	0.80	0.89

Table 2: Average values of the measured and calculated quantities in the set of all the samples
Tabela 2: Povprečne vrednosti izmerjenih in izračunanih količin za sklop vseh vzorcev

	$C_{av} \pm \sigma_C$	$I_H \pm \sigma_I$	$k_{ef} \pm \sigma_k$	$k^{(ref)}$ [13–15]
Al	0.0136 0.0029	1.352 0.162	0.294 0.046	0.12–0.92
Si	0.1910 0.0068	0.285 0.011	0.781 0.005	0.66–0.91
P	0.0141 0.0023	1.270 0.133	0.314 0.035	0.06–0.50
S	0.0136 0.0030	1.657 0.297	0.232 0.035	0.02–0.10
Ti	0.0951 0.0032	0.306 0.027	0.765 0.019	0.05–0.60
Cr	0.1758 0.0076	0.255 0.023	0.799 0.017	0.30–0.97
Mn	0.8232 0.0169	0.143 0.009	0.873 0.033	0.72–0.90

Table 2. It follows from this table that the dendritic heterogeneity of the slab decreases in this order of elements: sulphur, aluminium, phosphor, titanium, silicon, chromium and manganese, which has the lowest index of heterogeneity.

The dendritic heterogeneities of the analyzed elements are also expressed with the values of their effective partition coefficients for the individual samples as listed in **Table 1** and for the set of samples in **Table 2**. It is obvious that pair values of the index of dendritic heterogeneity and the effective distribution coefficient for the same element do mutually correspond. The fact is that the higher the value of a heterogeneity index, the lower the value of an effective partition coefficient and vice versa. The lowest value of the effective partition coefficient is found in sulphur and the highest value is found in manganese. It follows from **Table 2** that an effective distribution coefficient increases in this order of elements: S, Al, P, Ti, Si, Cr and Mn. All the analyzed elements segregate during the solidification into an inter-dendritic melt, and their partition coefficient is smaller than one.

For comparison, **Table 2** contains also the values of the partition coefficients found in literature.[13–15] It is obvious that our values of the effective partition coefficients, calculated according to the original model, are in good agreement with the data from the literature, with the exception of sulphur (and titanium). The reason for this difference is probably the method of calculating an effective partition coefficient – the value of this parameter is calculated from the concentration-data set measured on a solidified and cooled casting. Consequently, the effective partition coefficients calculated in this way inherently include both the effect of segregation in the course of alloy solidification and the effect of homogenization, occurring during the solidification as well as during the cooling of an alloy.

The presented methodology of an investigation into the chemical micro-heterogeneity makes it possible to study and to describe the micro-segregation behavior of the selected elements in the representative areas of a steel slab. Since a microprobe was used for the experimental investigation, the results have a high accuracy (even though an assessment with a microprobe is time-intensive and costly). The results, acquired in this way, can also provide the standards for another, faster and cheaper method for investigating the (micro)heterogeneity of a CC steel slab.[16]

4 CONCLUSIONS

The following main findings and results were obtained during an investigation into the chemical micro-heterogeneity of a CC steel slab:

- the dendritic heterogeneity of the accompanying elements and impurities is comparatively high;
- all the analyzed elements segregate during the solidification into an inter-dendritic melt, and their partition coefficient is smaller than one (concrete values of the partition coefficients for the analyzed elements and individual samples are given in **Table 1**, the average values for all the samples are given in **Table 2**);
- the dendritic heterogeneity decreases in the following order of elements: S, Al, P, Ti, Si, Cr and Mn;
- the effective partition coefficients calculated in this new way inherently include both the effect of segregation in the course of an alloy's solidification, and the effect of homogenization, occurring during the solidification, as well as during the cooling of an alloy.

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