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Microstructure evolution during the solidification of steel (Review)

D.M.STEFANESCU

In today's material world it is agreed that a complete understanding of the solidification path and of the resulting microstructure can only be obtained by treating the alloys as mathematical systems, followed by validation of the models through definitive experiments. This paper will attempt to review the main recent experimental and mathematical efforts directed to the understanding of microstructure evolution in steel.

(cf. *ISIJ Int.*, **46** (2006), 786)

Liquid–solid interface free energies for metals from free-volume method and interface structural model

K.NAKAJIMA

The thermodynamic approximate-expression for liquid–solid interface free energy which has its origin in the loss of configurational entropy due to the adjustment of the liquid to a boundary was derived. Triangular-square-pentagonal lattices were proposed for a structural model of the liquid–solid interface. Calculated values from the thermodynamic approximate-expression and the interface structural model showed a fair agreement with previous experimental data.

(cf. *ISIJ Int.*, **46** (2006), 795)

Effect of catalyst on heterogeneous nucleation in Fe–Ni–Cr alloys

K.NAKAJIMA et al.

In order to elucidate the nature of heterogeneous nucleation, a differential scanning calorimetry (DSC) thermal analysis of Fe–Ni–Cr alloys (Ni+Cr content=30 mass% (constant); Ni content: 7.5 to 29.3 mass%) containing TiN and Al_2O_3 was conducted. Then, special attention was paid to the difference in the phase of the primary crystal nucleated by the triggering effect of a catalyst (nucleating agent). The solidification and transformation mode appearing during cooling in these alloys is classified into three cases: F mode, FA mode, and A mode. The change of modes and the critical undercooling (ΔT) depend on the kind of catalyst used as well as on the chemical composition. In addition, in spite of the kind of primary crystal, the value of ΔT is always smaller in the order of TiN $<Al_2O_3$. These findings are the same as those for Fe–Ni alloy, although Fe–Ni–Cr alloys have the advantage that the increase of Cr content can trigger the crystallization of the primary crystal of the δ phase, which consequently can reduce ΔT and extend the region of low ΔT. The total concentration of catalyst molecules (C_1), as well as the interface free-energy ratio ($(\gamma_{CL}-\gamma_{SC})/\gamma_{LS}$), is one of the most significant factors in explaining undercooling for heterogeneous nucleation. $(\gamma_{CL}-\gamma_{SC})/\gamma_{LS}$ is related to the kind of catalyst used and the chemical composition, and C_1 is related to the crystallized content of catalyst. As a matter of fact, the number of catalysts supplied to the solidification front has a practical effect on the control of the solidification-structure.

(cf. *ISIJ Int.*, **46** (2006), 801)

Effect of oxide catalyst on heterogeneous nucleation in Fe–10mass%Ni alloys

K.NAKAJIMA et al.

In order to elucidate the nature of heterogeneous nucleation, a differential scanning calorimetry (DSC) thermal analysis of Fe–10mass%Ni alloys containing oxide catalysts was conducted. For all oxide catalysts, the maximum frequency in the particle-size distributions diminishes and the modal value increases with a decrease in the amount of deoxidizers or with an increase in the elapsed time after deoxidizer addition. That is, the number of smaller particles decreases, while the number of larger particles increases. In proportion to this change of the particle-size distribution, the critical undercooling (ΔT) increases. For the same amount of deoxidizers and the same elapsed time, the value of ΔT for the primary crystal of the γ phase is smaller in the order of MgO, ZrO_2, Al_2O_3, and CaO–Al_2O_3. Oxide catalysts grow by Ostwald ripening, therefore the growth can be controlled by the diffusion of oxygen. Thus, the decrease of the soluble oxygen content by strong deoxidizers results in the inhibition of particle growth.

(cf. *ISIJ Int.*, **46** (2006), 807)

Some aspects on grain refining additions with focus on clogging during casting

M.ANDERSSON et al.

Some ideas of how to study optimum conditions for implementation of grain refining in liquid steel processing with focus on how to avoid clogging are discussed. It is assumed that the inclusions most beneficial for grain refining are known from studies by physical metallurgists. The challenge for a process metallurgist is how to provide a homogeneous distribution of grain refiners at the onset of solidification. Four different ways of providing information to succeed with this are discussed. Thermodynamic modeling can be used to predict what additions to make to create potential grain refiners, if relevant thermodynamic data is available. Mathematical fluid-flow modeling can be used to study where to add potential grain refiners. It is discussed that the tundish is the most appropriate reactor to add grain refiners, since enough time is given to a complete mixing of the grain refiner into the steel before the steel enters the mold. By using the scanning laser microscopy technique it is possible to study which potential grain refiners has the lowest attraction forces between each other. This is important in order to minimise growth of inclusions when they collide during transport in the tundish, which can lead to the formation of larger inclusions that do not serve as useful grain refiners. Finally, it is suggested that laboratory experiments are carried out in order to study the tendency for nozzle clogging, before the use of grain refiners is tested in industrial scale.

(cf. *ISIJ Int.*, **46** (2006), 814)

Microstructure control of steels through dispersoid metallurgy using novel grain refining alloys

Ø.GRONG et al.

This paper describes how small inclusions (designated dispersoids) can be used to control the microstructure of steels. The term "dispersoids" refers to oxides, sulphides, nitrides and carbides which are in the 1 μm size range and capable of promoting grain refinement during solidification by a process of epitaxial nucleation or in the solid state through intragranular nucleation of ferrite. Such particles are sufficiently small to be harmless from a toughness point of view, but at the same time large enough to act as potent nucleation sites during phase transformation. The dispersoids can either be created by balanced additions of strong oxide and sulphide forming elements to an impure steel melt or be added directly into the liquid steel through a specially designed master alloy containing the nucleating particles. In both cases it is possible to manipulate the steel microstructure in a positive direction, but the latter method, involving the use of a master alloy, has probably a wider industrial application. The direction of the research now being undertaken at NTNU/SINTEF to make the grain refining alloys commercially available is briefly described towards the end of the paper.

(cf. *ISIJ Int.*, **46** (2006), 824)>

Effect of nonrandomly dispersed particles on austenite grain growth in Fe–10mass%Ni and Fe–0.20mass%C–0.02mass%P alloys

H.OHTA et al.

The fraction of deoxidation particles of MgO, ZrO_2 and Ce_2O_3 on austenite grain boundaries in an Fe–10mass%Ni or Fe–0.20mass%C–0.02mass%P alloy has been measured as a function of dissolved Ce content. The fraction of particles on grain boundaries, Φ_A, which is defined by the ratio of the number of particles at the grain boundaries per unit area and the number of particles at the grain boundaries and the interior of the grain per unit area and the Φ_A value at random dispersion, $\Phi_{R(2\text{-}D)}$, attend the steady state within 60 min holding at 1 673 K. The Φ_A and $\Phi_{R(2\text{-}D)}$ values increase with the addition of very small amount of dissolved Ce and thereafter are independent of dissolved Ce content. The $\bar{D}_A/\bar{d}_A$ (limiting mean grain diameter/mean particle diameter) ratios decrease with an increase in Φ_A for a given volume fraction of particles.

(cf. *ISIJ Int.*, **46** (2006), 832)

Refinement of solidification microstructure and austenite grain by fine inclusion particles

H.SUITO et al.

The effect of deoxidation products of Ce_2O_3, ZrO_2 and MgO particles on solidification microstructure has been studied in Fe–10mass%Ni, Fe–0.20mass%C–0.02mass%P and Fe–0.50mass%C–1mass%Mn alloys. The degree of the equiaxed crystallization is explained by the lattice misfit parameter between γ (or δ)-Fe and oxide. The single-phase solidification microstructure of Fe–10mass%Ni and Fe–0.50mass%C–1mass%Mn alloys is well related to austenite grain boundaries under the inhibition of grain growth by pinning. The correspondence between solidification structure and initial austenite grain has been studied in two-phases solidification of Fe–0.15 (or 0.30)mass%C–1mass%Mn–1mass%Ni

alloy. The γ-grain size decreases with decreasing the lattice misfit parameter between γ-Fe and oxide and increases with decreasing the Zener pinning force. The number of γ-grains to that of primary δ-grains per unit area in a cross section increases with decreasing the aforementioned lattice misfit parameter, indicating that more than one nucleation event per δ-grain occurs at δ-ferrite grain boundary during δ to γ transformation.

(cf. *ISIJ Int.*, **46** (2006), 840)

"*In-situ*" observation of the δ/γ phase transformation on the surface of low carbon steel containing phosphorus at various cooling rates

Z.LIU et al.

In this paper, the solid δ/γ phase transformation is observed "*in-situ*" on the surface of low carbon steels containing different phosphorus concentrations by the Confocal Scanning Laser Microscope (CSLM) at various cooling rates. The effects of phosphorus and cooling rate on the δ/γ phase transformation are discussed based on the experimental results and mathematical calculation. Phosphorus is shown to decrease the T_{A4} temperature and to increase the T_{A3} temperature at various cooling rates. This effect is enhanced by the redistribution of phosphorus from the γ phase to the δ phase during the transformation. Some retained δ phase is kept until the γ/α phase transformation in steel containing high phosphorus (0.2% P). The retained δ phase could retard the γ grain growth and promote the α phase precipitation. At the slow cooling rate, the γ cells appear first from the triple points or δ grain boundaries and then spread with finger-like patterns. While at the rapid cooling rate, the γ cells appear first from the δ grain boundaries with sword-like patterns, and spread sharply into both sides of initial δ grain boundary.

(cf. *ISIJ Int.*, **46** (2006), 847)

Prediction of prior austenite grain size of high-phosphorous steels through phase transformation simulation

H.S.KIM et al.

The effects of phosphorous content and cooling rate on the phase evolution of low carbon steels were analyzed by DICTRA simulation focusing on the micro-segregation behavior of phosphorous during solidification and subsequent cooling process. Through the phase transformation simulation, the effects of metallurgical parameters such as P content, cooling rate, and primary dendrite arm spacing on the starting temperature of austenite grain growth were clarified. Using the values of austenite grain growth starting temperature calculated by the phase transformation simulation, prior austenite grain size of low carbon steels were estimated based on a classical grain growth modeling in a P content range from 0.01 to 0.20 mass% and in a wide cooling rate range from 1.7 to 800 K s^{-1}. The prior austenite grain size predicted with the present approach showed good agreement with a group of selected experimental data of 100 mm thick slabs and 2 mm thick strips.

(cf. *ISIJ Int.*, **46** (2006), 854)

Crystal alignment of Sn–Pb alloy by controlled imposition of a static magnetic field and an alternating electric current during solidification

M.USUI et al.

In this study, a new process for a crystal alignment of an alloy during solidification has been proposed in which the imposing periods of a static magnetic field and an alternating current are controlled. In the initial stage of the solidification both the magnetic and electric fields are imposed on the alloy to break dendrites into pieces and to spread them to the whole area of the sample. In the next stage, only the static magnetic field was applied for the sample. The function of the static magnetic field in this stage is not only the rotation of the crystals to magnetically stable direction but also the suppression of the disturbance such as liquid motion. The principle of this process was experimentally confirmed by using a Sn–10mass%Pb alloy. In the X-ray diffraction pattern of the sample solidified without the static magnetic field, the first and second highest peaks were (101)-plane and (200)-plane. That is, the crystal direction is random. On the other hand, only the peaks corresponding to a,b-plane were observed in the sample solidified under the imposition of the controlled electromagnetic field. Therefore, this process is useful for the crystal alignment of alloy.

(cf. *ISIJ Int.*, **46** (2006), 859)

In-situ observation of growth and melting of a solid particle using transparent organic alloys

H.ESAKA et al.

Seed crystal for equiaxed grain may be suffered from the temperature change in the liquid phase. Seed crystal may grow and/or melt depending on the thermal field. In order to analyze the growth and melting of a solid particle, *in-situ* observation using succinonitrile-water alloys with the newly constructed experimental equipment have been performed. In the central region of the ring heater, a small spherical solid particle is held for a while. When the voltage for the ring heater was abruptly changed, the solid particle grew or melted. The morphological change was recorded and analyzed.

In case of growth, it indicated that the solid/liquid interface is dendritic. After stopping growth, the solid phase became round if the solute content is low. On the other hand, if the solute content is high, solid/liquid interface remained dendritic.

In case of melting, the solid/liquid interface is complex. If the solid phase is round after growth, it melted remaining round. If the solid/liquid interface was dendritic after growth, dendrite arms became slender and the tip of dendrite became pointed. Some secondary dendrite arms may have been detached.

It has been found that the melting velocity is lower than the growth velocity. Because of the difference in solid/liquid interfacial morphology and because of the difference in the traveling velocity of solid/liquid interface, the kinetics of growth and melting are different. One of the important reasons is the difference in operating point for growth and melting. In case of growth, the operating point is dendrite tip. On the other hand, in case of melting, it is rather wide area, which is inside of the envelope of the tips of the solid phase.

(cf. *ISIJ Int.*, **46** (2006), 864)

Fabrication of TiB_2 particle dispersed FeAl-based composites by self-propagating high-temperature synthesis

K.MATSUURA et al.

FeAl–TiB_2 composites have been produced from mixtures of Fe, Al, Ti and B powders using the Self-propagating High-temperature Synthesis (SHS or combustion synthesis) method. When the powder mixture was heated in vacuum to approximately 900 K, an abrupt increase in temperature was observed, indicating that the SHS reaction occurred in the powder mixture. The treating time from the start of heating to the end of the exothermic reaction was only approximately two minutes. X-ray diffraction analyses revealed that the SHS sample consisted of only FeAl and TiB_2 without any elemental metals and any other compounds. Metallographic investigations using a scanning electron microscope and an electron probe microanalysis revealed that fine TiB_2 particles were dispersed in FeAl matrix phase. As the volume fraction of the TiB_2 particles was increased from 0.3 to 0.8 by controlling the powder mixture composition, the average TiB_2 particle size increased from 1 to 7 μm and the average Vickers hardness of the composites increased from 800 to 1 600.

(cf. *ISIJ Int.*, **46** (2006), 871)

Grain refinement and improvement in mechanical properties of Nb–Al–Si intermetallic alloys

K.MATSUURA et al.

Nb–Al–Si intermetallic alloys having submicron crystal grains have been produced using the self-propagating high-temperature synthesis (SHS, or combustion synthesis) method followed by the bead milling technique and the spark plasma sintering (SPS) method. The intermetallic alloys were combustion-synthesized from elemental powders of niobium, aluminum and silicon, and then ball-milled and bead-milled to reduce the alloy powder particle size. The milled alloy powder was consolidated using the SPS method with a sintering time of 300 s at a sintering temperature of 1 373 K. The increase in milling time reduced the grain size of the sintered alloy. Particularly, the grain size was dramatically reduced when zirconia beads of a 0.2-mm diameter were used after milling with zirconia balls of a 10-mm diameter. The Vickers hardness, bending strength and fracture toughness of the sintered alloys increased with the decrease in grain size.

(cf. *ISIJ Int.*, **46** (2006), 875)

Modeling of macrosegregation and solidification grain structures with a coupled cellular automaton—finite element model

G.GUILLEMOT et al.

A coupled Cellular Automaton (CA)–Finite Element (FE) model is presented for the prediction of solidification grain structures coupled with the calculation of solid and liquid flow induced macroseg-

regation. The model is applied to simulate the solidification of a Pb–48wt%Sn alloy in a rectangular cavity cooled down from only one of its vertical boundaries. The algorithm and the numerical implementation of the coupling between the CA and FE methods are first validated by considering a single grain developing with no undercooling. Such a CAFE simulation is shown to retrieve the solution of a purely FE method simulation for which the grain structure is not accounted for. Several applications of the model are then presented to quantify the effects of the grain structure on the final macrosegregation map. In particular, the effect of the undercooling of the columnar front, the presence of equiaxed grains nucleated in the undercooled liquid, as well as the transport and sedimentation of equiaxed grains are investigated. Although good validation is reached when comparing computed and measured segregation profiles available in the literature for the chosen configuration, it is concluded that refined experimental data are required to further validate the predictions of a coupled CAFE model.

(cf. *ISIJ Int.*, **46** (2006), 880)

Prediction of casting structure in aluminum-base multi-component alloys using heterogeneous nucleation parameter

Y.NATSUME et al.

Heterogeneous nucleation rates in solidifying aluminum-base multi-component alloys (AC2A, AC2B and AC8C commercial alloys) were determined as the form of the nucleation parameter. Unidirectional solidification experiments were carried out using the multi-component alloys and the nucleation parameters were determined by simulating the macrostructure similar to the experimentally observed one with a PF-CA model, which is a model developed by coupling a cellular automaton (CA) method with a phase-field (PF) method. A conventional casting experiment for the multi-component alloys was carried out, and prediction of the macrostructure of the castings with the PF-CA model has been carried out using the determined nucleation parameters from the unidirectional solidification. In the case of the AC2A commercial alloy, the simulated macrostructure was in good agreement with the experimentally observed one. In the case of the AC2B commercial alloy, although the simulated macrostructure near the mold wall was different from the experimentally observed one, the size of inner equiaxed crystals was similar to that observed in the experiment. In the case of the AC8C commercial alloy, the simulated macrostructure was not similar to the experimentally observed one. The disagreement between the results of the experiment and simulation might be due to a multi-phase solidification manner in the AC8C alloy.

(cf. *ISIJ Int.*, **46** (2006), 896)

Numerical simulation of solidification structure formation during continuous casting in Fe–0.7mass%C alloy using cellular automaton method

M.YAMAZAKI et al.

A numerical model was developed for the simulation of solidification structure formation during the continuous casting process of an Fe–0.7mass%C alloy. In this model, the cellular automaton method was combined with heat transfer calculation during the continuous casting process. The effect of electromagnetic stirring (EMS) during the continuous casting process was introduced as an increase in thermal conductivity in liquid. Furthermore, the effect of fragmentation of dendrites due to fluid flow during EMS was taken into account in the model as an increase in the formation of crystals. Simulations of grain structure formation in continuously cast billets with and without EMS were carried out, and the degree of fragmentation was evaluated from a comparison between experimentally observed and simulated macrostructures of the billets.

(cf. *ISIJ Int.*, **46** (2006), 903)

Dendrite growth model using front tracking technique with new growth algorithm

M.NAKAGAWA et al.

A numerical model using a modified front tracking technique has been developed to simulate dendrite growth during the solidification of binary alloys. Diffusion in liquid and solid, mass conservation at the solid/liquid interface and local equilibrium at the solid/liquid interface with consideration of curvature undercooling were solved to determine the position of the solid/liquid interface. Preferential crystallographic orientation of a dendrite was taken into account by introduction of a modified growth technique. The growth process of a dendrite having an arbitrary preferential crystallographic orientation has been simulated in 2D using the developed model. Simulations were carried out for the growth of many dendrites in an aluminum–silicon binary alloy with continuous cooling and isothermal solidification conditions. The amount of eutectic formed in aluminum–silicon alloys with different Si content was estimated from the simulation. The estimated amounts of eutectic fell between the values predicted from the Scheil equation and the equilibrium lever rule. This result demonstrates the capability of the model for predicting grain macrostructure of alloy castings by taking into account information such as dendrite morphology, amount and distribution of the eutectic phase and microsegregation.

(cf. *ISIJ Int.*, **46** (2006), 909)

Simulation of microstructure of as-cast steels in continuous casting

S.LOUHENKILPI et al.

Prediction and control of steel microstructure during and after the continuous casting process is an extremely important task for steel producers making special steels with high quality demands. Continuous casting is a very complex process with series of parallel phenomena with heat and mass transfer, solidification and phase transformations. As a long-term project the authors have proceeded by developing first a two-dimensional heat transfer model, then a three-dimensional and finally, a dynamic three-dimensional heat transfer model to simulate the continuous casting process. A special solidification model was developed as well, and coupled with the heat transfer model. Models were experimentally validated and numerous industrial cases were calculated and compared with measurements. The models seemed to predict quite accurately the phase transformations and micro-structural features like dendrite arm spacing and austenite grain size, phase fractions and hardness throughout the whole as-cast strand.

(cf. *ISIJ Int.*, **46** (2006), 914)

Prediction of equiaxed crystal ratio in continuously cast steel slab by simplified columnar-to-equiaxed transition model

H.SHIBATA et al.

A simplified prediction model of the equiaxed crystal ratio (ECR) in continuously cast slabs of ferritic stainless steel was investigated based on the columnar to equiaxed transition (CET) model proposed by J. D. Hunt. The present model assumes that CET occurs when a parameter $G/V^{1/2}$ at a solid fraction of 0.3 is smaller than a critical value, C_{ET}. This model can explain comparatively well the effects of the casting speed, melt superheat, steel composition, intensity and position of the electromagnetic stirring (EMS), and secondary cooling intensity on measured ECR. The calculated results also show that an optimum EMS position and casting speed for maximizing ECR exist. Moreover, it was found that there is a proportional relationship between the best-fit values of C_{ET} and $N_0^{1/3}C_0^{1/2}$ calculated from measured data. This means that the simplified Hunt model is applicable to predict ECR in continuously cast slabs. The mechanism by which equiaxed crystal bands are generated is also discussed in relation to the behavior of $G/V^{1/2}$.

(cf. *ISIJ Int.*, **46** (2006), 921)

Micro-segregation on the mono-variant line of an iron–carbon–chromium ternary alloy

T.HIMEMIYA

To examine an effect of diffusion in the solid on the micro-segregation on a mono-varinat line, a directional solidification experiment has been carried out in an iron–carbon–chromium ternary alloy. In an iron–carbon–metal ternary alloy, carbon is an interstitial solute in an iron-base solution (austenite or ferrite) and the diffusivity in the solution is not negligible, while the third metallic element in the iron-base solution is usually substitutional solute and its diffusivity is negligible compared with that of carbon. The second phase of the ternary alloy is usually a kind of carbide, and the diffusivity of carbon or the third metallic element can be neglected because of the strength of the bonding forces of the atoms. In such a situation with dendritic-eutectic mode, a micro-segregation model on the mono-variant line has been introduced, and it has been predicted that the progress of the solidification might terminate before reaching the three-phase eutectic point. If we assume a Scheil-type model of micro-segregation on a mono-variant line, the composition of the residual liquid will reach the terminal (for example, three-phase eutectic) point.

To confirm this prediction, an experiment has been carried out in an iron–carbin–chromium alloy.

The initial composition is 3.17 mass% C and 25.6 mass% Cr and very near the eutectic valley of austenite–$(Fe, Cr)_7C_3$. With no diffusion of carbon in the austenite phase, the solidification will change to austenite–$(Fe, Cr)_3C$ eutectic reaction through the peritecto-eutectic point. With the effect of carbon, using the model, the solidification will end before reaching the peritecto-eutectic point and $(Fe, Cr)_3C$ formed during solidification will not be found. The metallographical observation revealed the exsistence of $(Fe, Cr)_7C_3$ phase but did not reveal the exsistence of $(Fe, Cr)_3C$ phase. The EPMA measurement between the dendritic arms showed that the measured minimum chromium compositions inside the austenite agree with the predicted values within an experimental error and uncertainties of parameters of the system. The identificatin of the phases by using XRD indicated that austenite–$(Fe, Cr)_3C$ eutectic did not form, as was predicted. These results suggest the validity of the model of micro-segregation on the mono-variant line in an iron–carbon–metal ternary system.

(cf. *ISIJ Int.*, **46** (2006), 931)