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THE OPTIMISATION OF TITANIUM AND NITROGEN CONCENTRATION IN MICRO-ALLOYED STEEL

OPTIMALIZACJA STĘŻENIA AZOTU I TYTANU W STALI MIKRO-STOPOWEJ

The paper deals with the control of the concentrations of titanium and nitrogen content in micro-alloyed steel with the aim of preserving sufficient amounts of these components for precipitation of relevant amount of TiN inclusions in austenite. Fine TiN inclusions inhibit the growth of austenite grains during soaking prior to hot rolling. The analysis of three stages of secondary metallurgy treatment: deoxidization with aluminum, titanium addition and cooling down to liquidus temperature was based on the parameters of thermodynamic equilibrium between metallic phase and non-metallic phases present in the system. The equilibrium compositions of phases were calculated by means of the FactSage software. The low alloyed carbon steel containing 0.02 % C, 1.5 % Mn and 0.2 % Si was the subject of calculations. It was determined that deoxidization by means of aluminum reduces the oxygen concentration below 20 ppm. The TiN addition causes the formation of solid TiN and the modification of composition of liquid oxide precipitates with dissolved Ti_2O_3 . The composition of obtained phases as well as the titanium distribution were determined for various initial nitrogen contents, steel deoxidization levels and titanium additions. It was stated that the most effective use of titanium from the view point of TiN formation in austenite appears at relatively low nitrogen concentration in steel, approximately 25 ppm.

Keywords: micro-alloyed steel, TiN precipitation, structure control, inter-phase equilibrium

Praca analizuje kontrolę stężenia tytanu i azotu w stalach mikro-stopowych podczas ich przygotowania do ciągłego odlewania pod kątem zachowania takiej ilości tych składników, która pozwoli na uzyskanie odpowiedniej ilości wydzieleni TiN w austenicie. Drobne wtrącenia TiN hamują wzrost ziaren austenitu podczas nagrzewania przed walcowaniem na gorąco. Analiza trzech etapów pozapiecowej obróbki stali: odtleniania glinem, wprowadzania tytanu oraz schłodzenia do temperatury likwidus oparta jest na wyznaczeniu parametrów termodynamicznej równowagi między fazą metaliczną i fazami niemetalicznymi obecnymi w układzie. Równowagowe składy faz zostały obliczone przy pomocy pakietu programów FactSage. Stal mikro-stopowa zawierająca 0.02 % C, 1.5 % Mn oraz 0.2 % Si była przedmiotem obliczeń. Stwierdzono, że odtlenianie przy pomocy glinu redukuje stężenie tlenu w ciekłej stali poniżej 20 ppm. Wprowadzenie tytanu powoduje tworzenie stałego TiN oraz modyfikację składu ciekłej fazy tlenkowej poprzez rozpuszczanie w niej powstającego Ti_2O_3 . Skład chemiczny otrzymanych faz oraz rozdział tytanu między nie został wyznaczony dla różnych początkowych stężeń azotu, stopni odtlenienia stali oraz dodatków tytanu. Stwierdzono, że najefektywniejsze wykorzystanie wprowadzonego do stali tytanu z punktu widzenia wytworzenia TiN w austenicie występuje przy względnie niskim stężeniu azotu w stali, w przybliżeniu 25 ppm.

1. Introduction

Required mechanical properties of micro-alloyed steel containing titanium are obtained as a result of combination of two effects: preservation of small austenite grains during high temperature heating prior to the rolling operation and the precipitation strengthening at lower temperatures [1]. The precipitation strengthening may be put into effect by several means, i.e. the formation of nitrides, carbides or carbo-nitrides of vanadium, niobium or titanium. The control of austenite grains, however, may be executed only with TiN precipitates.

This results from the thermodynamic conditions of corresponding compounds formation from liquid or solid metallic solutions. The main task of process engineer is the arrangement of appropriate micro-alloyed steel composition at the beginning of solidification. Two factors must be taken into consideration: the concentration of titanium and nitrogen in steel has to be sufficient for formation of fine TiN in austenite, and excess amounts of titanium and, to some extent nitrogen should be avoided. Excess titanium results in formation of coarse TiN grains during steel solidification, which may act as the sources of cracks in the product [2]. The aim of the present work

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is to outline the procedure of calculation of optimum amounts of aluminum, nitrogen and titanium added to liquid steel. It must be kept in mind that TiN which forms in liquid steel above the liquidus temperature is being at most removed and is thus useless for austenite grains control. The titanium which reacts with dissolved oxygen and forms Ti_2O_3 , which participates in liquid or sometimes solid oxide solution, is also excluded from structure improvement action.

2. The procedure of calculations

The typical micro-alloyed steel is the subject of considerations in the present work. Its basic composition prior to the final treatment (aluminum and titanium additions) is as follows: 0.02 % C, 1.5 % Mn, 0.2 % Si, 0.005 % S, 0.05 % P.

This steel contains also variable concentrations of oxygen and nitrogen. The analysis in the present work regards three steps of final treatment of steel prior to its casting: deoxidization with aluminum at 1810 K, subsequent titanium addition at 1805 K and cooling the steel in the tundish and in casting mold down to liquidus temperature 1790 K. At each step the thermodynamic equilibrium parameters: masses and compositions of existing phases were calculated. After deoxidization at 1810 K the system consisted of liquid steel and liquid oxide solution. The oxide solution was excluded from further calculations, i.e. it was assumed that it was removed from steel. The remaining steel phase corresponded to the system composition, to which titanium was added at 1805 K. As a result, three phases were present in the system: liquid steel, liquid oxide solution and solid TiN. Again the remaining steel phase was taken as the entire system for new step of calculations, while liquid oxide and solid TiN were excluded from considerations. Then the cooling from 1805 K to 1790 K (assumed as liquidus temperature) was considered and the equilibrium composition of the system at 1790 K calculated. The calculations were carried out by means of the FactSage software [3].

3. The results of calculations

3.1. Deoxidization with aluminum

The proportion between amount of introduced aluminum and oxygen concentration in liquid steel is the crucial factor, decisive in the result of deoxidization. In the present work the initial oxygen content, prior to deoxidization, of 100, 150 and 200 ppm were considered. The calculations were carried out for the amounts

of added aluminum in the range 30 – 150 ppm. The amounts of added aluminum, like these of added titanium were expressed in the present work in ppm referring to initial mass of steel prior to Al or Ti addition. The results of calculations for 1810 K were presented in Figs 1 and 2. Fig. 1 demonstrates how the concentrations of oxygen and aluminium dissolved in liquid steel vary with increasing amount of added aluminum. It may be observed, that introduction of appropriate amount of aluminum results in approximately constant final concentrations of oxygen and aluminum in steel regardless on the initial oxygen content. Final oxygen concentration is below 20 ppm, while corresponding aluminum concentration – above 10 ppm. It results also from Fig. 1 that addition of ca 100 ppm aluminum is sufficient to achieve this result.

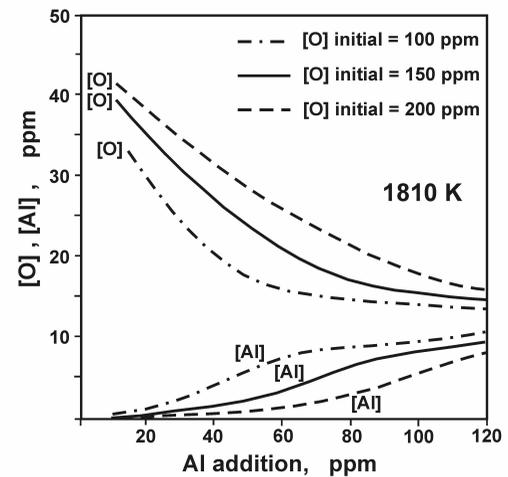


Fig. 1. Concentration of oxygen and aluminum in steel after aluminum deoxidization at 1810 K

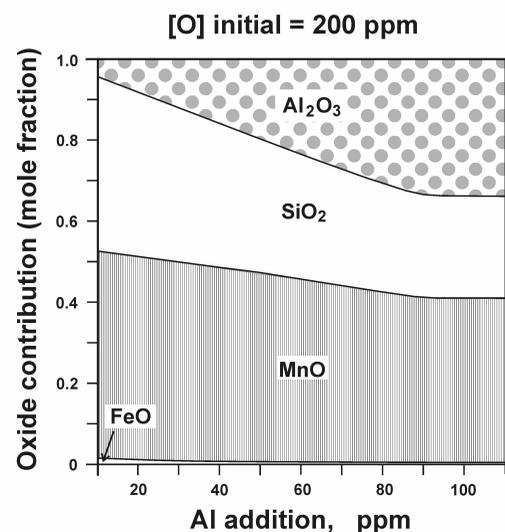


Fig. 2. The composition of liquid oxide phase after aluminum deoxidization at 1810 K

Fig. 2 presents the evolution of the composition of liquid solution which forms after introduction of increasing Al additions. The main component of oxide phase is the manganese oxide. With increasing amount of added aluminum the contribution of Al_2O_3 grows strongly at the beginning, and then the Al_2O_3 content tends to stabilize. The final concentration is $X_{\text{Al}_2\text{O}_3} = 0.33$. The oxide solution contains also small amount of FeO, slightly exceeding $X_{\text{FeO}} = 0.01$. The prevailing contribution of MnO and SiO_2 causes that the oxide solution is liquid, as the eutectic temperature in MnO-SiO₂ binary system is as low as 1200 K at $X_{\text{MnO}} = 0.57$.

3.2. Titanium addition

Titanium introduced into steel at 1805 K reacts both with oxygen and nitrogen dissolved in steel. Thus titanium is present in the system either in liquid oxide solution in the form of Ti_2O_3 [4] or in the form of solid TiN, which constitutes the separate phase. Some amount of titanium dissolves in steel. In the present work the equilibrium compositions and mass of liquid steel, liquid oxide solution and solid titanium nitride were calculated. The calculations were carried out for two values of nitrogen concentrations in steel: 25 ppm and 50 ppm. It was assumed that the required concentration of nitrogen had been settled in preceding stages of steel treatment and it did not vary significantly during aluminum deoxidization. Thus nitrogen becomes active steel component only after titanium addition. The calculations show that the amount of aluminum nitride produced during aluminum deoxidization is negligibly small.

The amount of added titanium considered in present calculations corresponds to its concentration in the range 50 – 150 ppm. The results of calculations of equilibrium concentrations of titanium and nitrogen dissolved in liquid steel are presented in Figs. 3 and 4 for two levels of steel deoxidization. The steel labelled no 1 contained initially 100 ppm of oxygen, and its deoxidization was carried out by means of aluminum amount corresponding to 100 ppm. In the case of steel labelled no 2 the initial oxygen concentration was also 100 ppm, while the amount of aluminum added was only 30 ppm. It may be noticed that the concentrations of titanium and nitrogen in both cases considerably differ in dependence on initial concentration of nitrogen in steel. For initial nitrogen concentration 50 ppm the calculated values of [Ti] are approximately 3 times higher than these for initial nitrogen concentration 25 ppm.

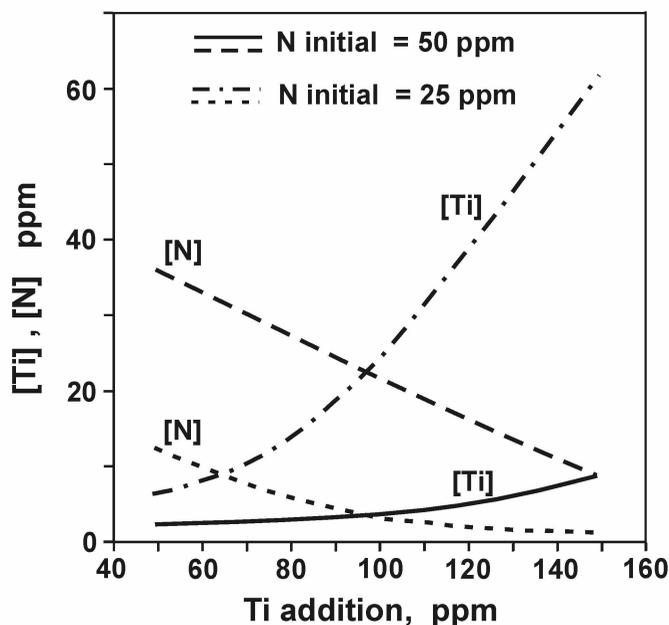


Fig. 3. The concentration of titanium and nitrogen in liquid steel no 1 [100 ppm O, 100 ppm Al added] at 1805 K in dependence of the amount of titanium added

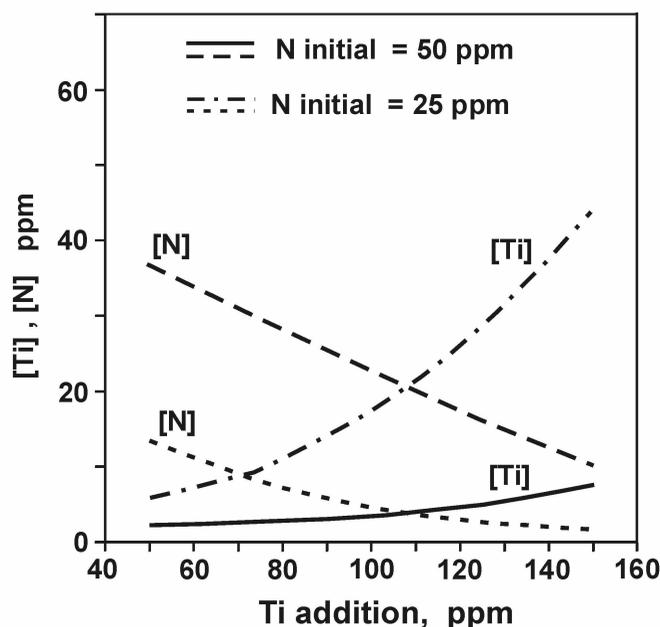


Fig. 4. The concentration of titanium and nitrogen in liquid steel no 2 [100 ppm O, 30 ppm Al added] at 1805 K in dependence of the amount of titanium added

The influence of amount of aluminum used for deoxidization as well as initial oxygen content is also well marked in the results of calculations. In the steel no 1 the maximum concentration of dissolved titanium reaches 60 ppm, while in the steel no 2 – merely 40 ppm.

Figures 5 and 6 present the composition of liquid oxide phase, which forms as a result of titanium ad-

dition. They refer to the steel no 3, which contained initially 150 ppm of oxygen and was deoxidized with aluminum in amount equivalent to 50 ppm. Fig. 5 and 6 present the results for the steel of initial nitrogen content 50 ppm and 25 ppm, respectively. The main component of liquid oxide is MnO, concentration of which exceeds $X_{\text{MnO}} = 0.5$ in both cases. SiO_2 is next in order with the maximum concentration $X_{\text{SiO}_2} = 0.43$. With increasing titanium addition SiO_2 is partly substituted with Ti_2O_3 . This effect is much stronger in steel of lower nitrogen concentration.

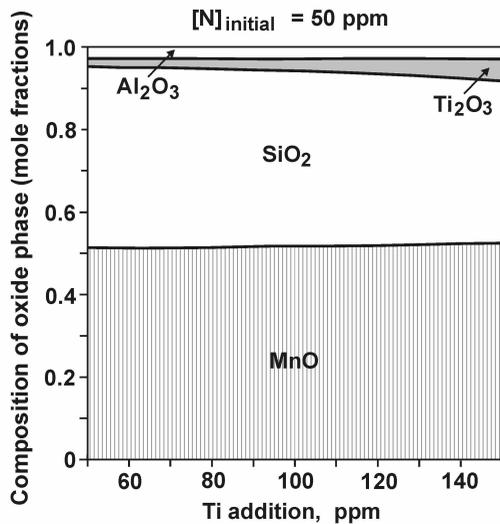


Fig. 5. Influence of the amount of added titanium in steel no 3 [150 ppm O, 50 ppm Al added] containing 50 ppm of nitrogen on the composition of liquid oxide phase at 1805 K

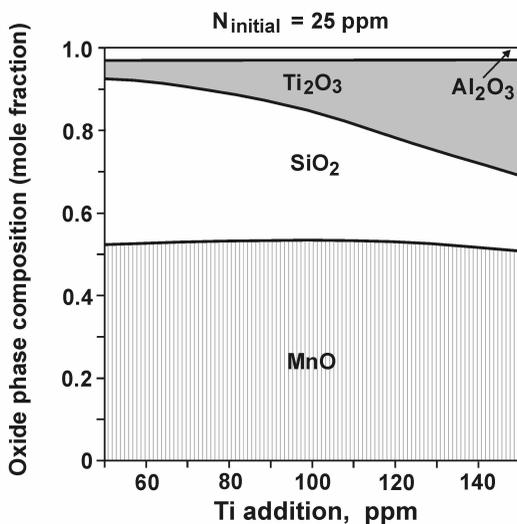


Fig. 6. Influence of the amount of added titanium in steel no 3 [150 ppm O, 50 ppm Al added] containing 25 ppm of nitrogen on the composition of liquid oxide phase at 1805 K

3.3. Temperature lowering from 1805 K down to 1790 K

Next it was calculated how the concentration of titanium and nitrogen in solution vary with temperature lowering down to the liquidus level – 1790 K. The maximum mass of titanium nitride which may be potentially obtained as a result of precipitation from solid solution due to strong decrease of temperature to the values below austenite region was also calculated.

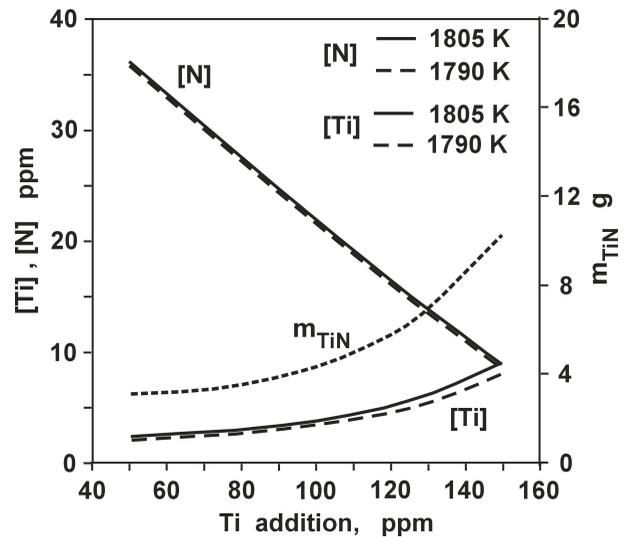


Fig. 7. Equilibrium concentrations of titanium and nitrogen in liquid steel nr 1 at the temperature 1805 K (heavy lines) and 1790 K (broken lines) and the maximal amount of potentially precipitated TiN. Initial concentration of nitrogen in steel 50 ppm

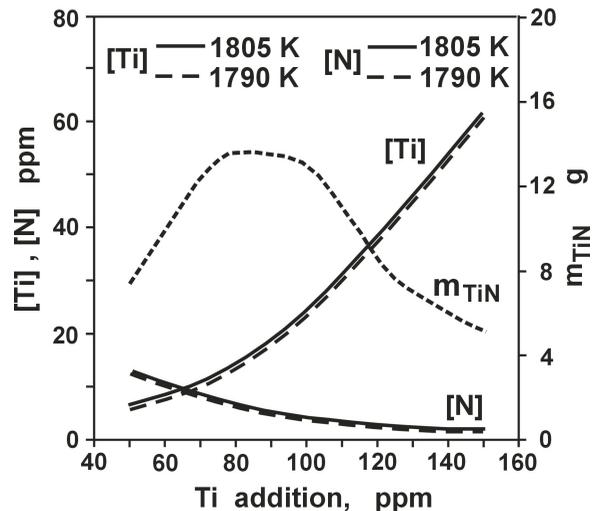


Fig. 8. Equilibrium concentrations of titanium and nitrogen in liquid steel nr 1 at the temperature 1805 K (heavy lines) and 1790 K (broken lines) and the maximal amount of potentially precipitated TiN. Initial concentration of nitrogen in steel 25 ppm

The results of calculations are demonstrated in Figs. 7 and 8. The results presented in Fig. 7 correspond to initial nitrogen concentration in steel 50 ppm. In this case the titanium introduced is predominantly combined with

nitrogen and the TiN precipitates thus formed float to the steel surface and are to the considerable extent assimilated in the top slag. It results from the above that at initial nitrogen concentration 50 ppm the effectiveness of titanium in TiN formation in the solidified steel is lower than at nitrogen initial concentration 25 ppm. At nitrogen concentration 50 ppm the maximum amount of TiN precipitated during solidification and subsequent cooling to ambient temperature is about 20 g (in 1 Mg sample), while at nitrogen concentration 25 ppm the maximum amount of TiN exceeds 50 g in 1 Mg steel sample.

The influence of initial nitrogen concentration in steel prior to titanium addition is illustrated also in Fig. 9, which presents the amount of titanium or nitrogen remained in solid steel (austenite) after formation of maximum amount of TiN precipitate. At initial nitrogen concentration 50 ppm considerable amount of this element remains in solution. This amount decreases if more titanium is added. When initial nitrogen concentration is 25 ppm, its amount present in solution is small, and finally it reaches zero if the amount of added titanium is 87 ppm. With larger amount of titanium added, its excess is present in solution and it grows with further titanium addition.

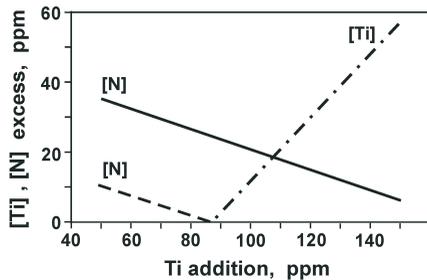


Fig. 9. Excess of titanium and nitrogen – hypothetical remainder in solid solution after TiN precipitation for steel nr 1. Heavy line – initial concentration of nitrogen – 50 ppm, broken line – 25 ppm

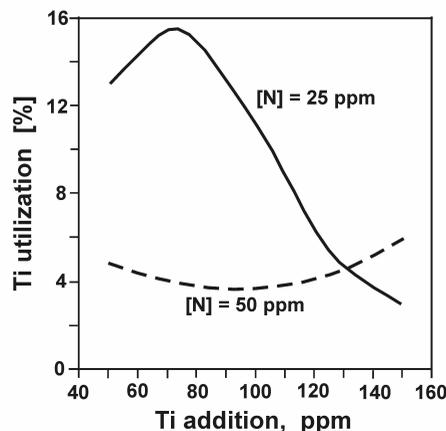


Fig. 10. Efficiency of Ti utilization in TiN formation in austenite in dependence of N concentration and Ti addition

The efficiency of titanium utilization as the

nitride-former in austenite was also deduced from the calculations. From the results presented in Fig. 10 it may be noticed that the level of nitrogen present in liquid steel prior to titanium addition has very strong influence on the titanium efficiency. At nitrogen concentration 50 ppm the titanium efficiency slightly exceeds 5% in relation to total titanium amount introduced to liquid steel. It only slightly depends on the amount of titanium added. At lower nitrogen concentration 25 ppm the titanium efficiency is much higher and it strongly depends on the amount of titanium added. The maximum of the curve appears about 80 ppm of titanium added. However, the level of nitrogen in micro-alloyed steel cannot be set at too low value for two reasons. The setting of too low nitrogen content may be difficult for technological reasons; it seems easier to introduce some amount of nitrogen during argon blowing. The other reason is that after TiN precipitation some amount of nitrogen should be still available in solid solution for the formation of vanadium or niobium carbides or carbonitrides.

The subsequent figures 11 and 12 present the example of titanium distribution between three phases: solid titanium nitride, liquid steel and liquid oxide solution. The data correspond to steel no 1. At higher initial nitrogen level the majority of introduced titanium precipitates as TiN, which is next removed from steel in casting tundish. No more than 6 % of titanium introduced dissolves in liquid steel, while only 0.5 % at most is present in oxide solution.

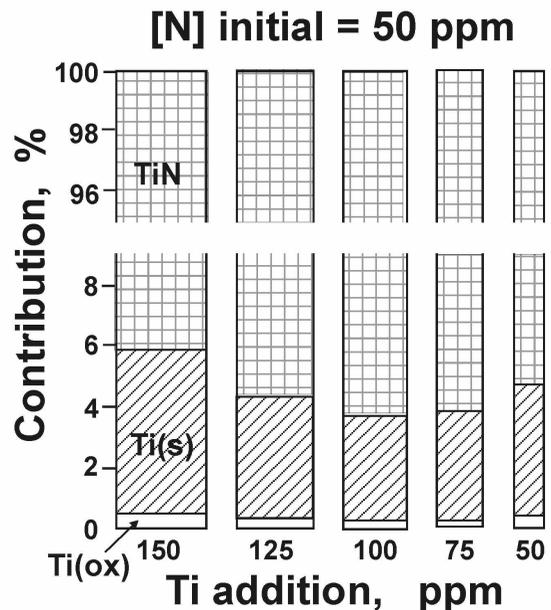


Fig. 11. Distribution of titanium between TiN, liquid steel – Ti(s) and oxide phase – Ti(ox) for steel no 1 at 1805 K in dependence of Ti addition. Initial N concentration 50 ppm

At lower nitrogen level in steel prior to titanium addition the titanium distribution between TiN, steel and

oxide phase is quite different. Much larger amount of titanium dissolves in liquid steel (41.2 mass % at most). Also the amount of liquid oxide solution is much larger, and consequently the titanium contribution in liquid oxides reaches 5 %. This difference shows very clearly, how important is the nitrogen level in optimisation of structure of steel through TiN precipitation in austenite.

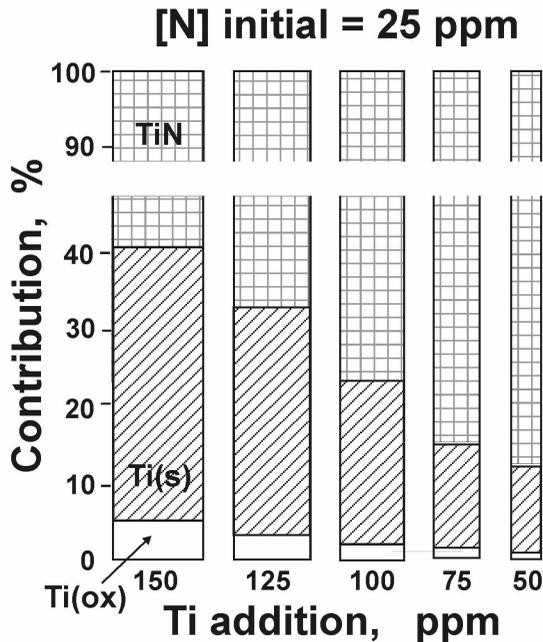


Fig. 12. Distribution of titanium between TiN, liquid steel - Ti(s) and oxide phase - Ti(ox) for steel no 1 at 1805 K in dependence of Ti addition. Initial N concentration 25 ppm

4. Conclusions

On the ground of the results obtained in the present work it may be stated that from the view point of TiN precipitates formation in austenite the proportion [Ti]:[N] = 3.42 is most favourable. This proportion may be reached e.g. at the nitrogen level in liquid steel 25 ppm and at the amount of above 80 ppm titanium added. The concentration of nitrogen in liquid steel set prior to titanium addition appeared to be very important factor, which is decisive for efficient use of titanium for struc-

ture control. Too high nitrogen level causes the losses of titanium in the form of TiN, which is removed from steel in the tundish. However, the nitrogen content cannot be too low, as proper control of austenite grains requires some minimum amount of TiN particles. After TiN precipitation some amount of nitrogen should also remain in solid solution to make possible nitrides or carbo-nitrides formation, which improve the mechanical properties through precipitation strengthening.

The appropriate deoxidization of steel is also of great importance, otherwise the considerable amount of introduced titanium goes into the oxide phase, as it may be seen at Figs 5 and 6. The calculations carried out in the present work are based on the assumption that liquid oxide precipitates formed at steel deoxidization by means of aluminium are entirely removed from steel. This is only an approximation. If the calculation of equilibrium includes participation of some amount of oxide phase with prevailing Al_2O_3 , the distribution of titanium between TiN and liquid oxide solution would vary.

The reliability of obtained results is strongly dependent on the quality of database of FactSage software. It especially regards the equilibrium solubility product [Ti]·[N]. However, the confrontation of the results obtained experimentally by Morita et al [5] and Kim et al [6] allows for considering the database as reliable one.

This work was financed by the Polish Ministry of Education and Science (contract nr 11.11.110.801 – AGH-UST Kraków)

REFERENCES

- [1] T. Senuma, ISIJ Intern. **42**, 1-12 (2002).
- [2] W. Yan, Y. Shan, K. Yang, Met. Materials Trans. A **37A**, 2147-2158 (2006).
- [3] <http://www.factsage.com>
- [4] J.-J. Pak, J.-O. Jo, S.-I. Kim, T.-I. Chung, S.-M. Seo, J.-H. Park, D.-S. Kim, ISIJ Intern. **47**, 16-24 (2007).
- [5] Z. Morita, T. Tanaka, T. Yanai, Met. Trans. B **18B**, 195-202 (1987).
- [6] W.-Y. Kim, J.-O. Jo, D.-S. Kim, J.-J. Pak, ISIJ Intern. **47**, 1082-1089 (2007).