

## Melting of Ni-Cr Cast Steel with Additions of Niobium and Titanium

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This study gives a compilation of values of the melting loss of individual elements present in creep-resistant 0.3 % C – 30 % Ni – 18 % Cr cast steel stabilised with niobium and titanium, produced from the melt made in an acid-lined induction furnace. The content of niobium in alloy varied from 0.0 to 2 %, and that of titanium from 0.0 to 1.2 % (%-wt). As-cast macro- and microstructures of this alloy were presented as well.

Keywords: Fe-Ni-Cr cast steel, melting, melting loss.

### 1. INTRODUCTION

Crucible induction furnaces are commonly used for melting of high-alloyed cast steels. The process usually consists in melting down some ferro-alloys, selected own alloyed scrap, and steel scrap, all in carefully matched proportions. Yet, in the acid process used most frequently because of a relatively low melting cost, one should be aware of the possible reduction of silica in furnace lining due to its reaction with some elements present in the charge. As a result, an undesirable change in the chemical composition of the melt, combined with reduced life of the lining take place. A definitely much lower cost of the silica refractories can, as a rule, compensate for the reduced life of lining, but keeping to the chemical composition previously established for an alloy may prove quite difficult, if not impossible at all [1 – 4].

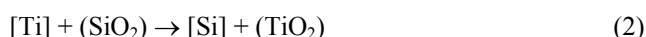
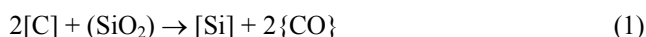
In this study, taking as an example eight melts of austenitic 30 % Ni – 18 % Cr cast steel with additions of niobium and titanium, the differences between the assumed and obtained values of the melting loss of the individual alloy constituents were stated. Melting was conducted in crucible induction furnace with acid lining.

### 2. MATERIAL AND EXPERIMENTAL

As a result of the studies done previously and described in [5], it was decided to use for parts of the carburising furnaces cast steel of the following composition (wt-%): 0.25 – 0.35 % C, 29 – 31 % Ni, 17 – 19 % Cr, 1.2 – 1.5 % Si, 0.5 – 0.8 % Mn, rest is iron and unavoidable impurities. As a next step in continuation of these studies, it was proposed to check the advisability of adding niobium and/or titanium to this cast steel and raising the level of silicon content. This trend in the studies is consistent with the present state of the art and forecasts of development made for alloys of this type [6, 7]. The test melts were made according to the plan of experiment [8], and after a preliminary analysis eight alloys were selected for further experiments. Below the melt history is given.

In designing of melts the following assumptions were made:

- the chemical composition of cast steel (%-wt) will be as follows:
  - constituents kept constant: C – 0.35 %, Mn – 0.8 %, Ni – 30 %, and Cr – 18 %,
  - variable constituents: silicon, niobium and titanium (see: Table 1).
- during melting, some undesirable changes in the chemical composition of the melt are to be expected, due to the reduction of silica present in the lining, caused mainly by two elements, viz. carbon and titanium. The respective reactions may proceed as indicated below [4]:



where [ ] is used to note the reagents present in molten metal, ( ) – solid reagents present in the lining or slag, { } – gaseous reagents.

In view of the above, the silicon content in the charge was reduced by 0.2 % in respect of the level anticipated previously, and a maximum admissible carbon content in alloy equal to 0.35 % was admitted (see Table 1).

- the value of the melting loss of the individual elements will be as follows: nickel and niobium – 0 %, chromium – 10 %, manganese – 20 %, and titanium about 45 % (the assumed values of titanium content are compiled in Table 1).
- before being introduced to the melt surface, both ferrotitanium and ferroniobium will be preheated to a temperature of 600 °C.

Melting was conducted in an IMSK 100 furnace with acid lining. Table 2 states the charge materials used for the melting and, as an example, the charge burden composition for alloy No. 8. The content in the charge of the first five constituents was kept constant and determined the level of the nickel, chromium and manganese additions required in the alloy, and to some extent also the content of carbon (0.26 %).

The content of the remaining ferroalloys was varying consistently in respect of the content of silicon, niobium and titanium adopted for this alloy. The charge was made up to the weight of 100 kg with low-carbon steel scrap.

The following procedure was adopted for the process of melting: the crucible was charged with pig iron, steel

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**Table 1.** Silicon, niobium and titanium content assumed in alloy (A) and in charge (B)

Alloy No		1	2	3	4	5	6	7	8
Si, %	A	1.83	1.39	1.22	1.83	1.22	1.95	1.83	1.22
	B	1.65	1.19	1.00	1.65	1.00	1.75	1.65	1.00
Nb, %	A	0.03	0.54	0.10	0.00	1.82	1.82	1.82	1.82
	B	0.03	0.54	0.10	0.00	1.82	1.82	1.82	1.82
Ti, %	A	0.03	0.30	1.18	1.18	0.05	0.05	1.18	1.18
	B	0.04	0.44	1.70	1.70	0.07	0.07	1.70	1.70

**Table 2.** Charge materials used for melting and charge burden composition for alloy No. 8

Charge materials	Chemical composition of materials, wt-%										Alloy No. 8	
	C	Si	Mn	P	S	Cr	Ni	Nb	Ti	Content in charge, wt-%		
Granulated Ni	–	–	–	–	–	–	98.7	–	–		30.4	
FeCr70-C	0.14	1.48	–	–	–	70.0	–	–	–		14.1	
Cr99	0.01	0.20	–	0.005	0.011	99.1	–	–	–		10.0	
Sorel pig iron	4.39	0.19	0.01	0.025	0.006	–	–	–	–		6.0	
FeMn80	1.40	1.10	81.6	–	–	–	–	–	–		1.1	
FeSi75	–	74.8	–	–	–	–	–	–	–		0.64	
FeNb70	0.10	1.20	–	0.130	0.040	–	–	67.5	–		2.7	
FeTi30	0.10	3.14	–	–	–	–	–	–	28.5		5.96	
Steel scrap	0.09	0.21	0.34	0.030	0.035	–	–	–	–		29.4	

**Table 3.** Chemical composition of melts, wt-%

Alloy No	C	Si	Mn	P	S	Cr	Ni	Nb	Ti
1	0.29	1.91	0.97	0.013	0.009	17.9	29.2	0.03	0.03
2	0.34	1.61	0.97	0.017	0.012	18.3	29.4	0.52	0.30
3	0.36	2.07	0.94	0.013	0.010	18.3	29.2	0.10	0.70
4	0.31	2.21	0.95	0.018	0.012	18.3	29.6	0.00	1.00
5	0.30	1.34	0.91	0.015	0.009	18.3	29.5	1.67	0.05
6	0.31	2.41	0.96	0.015	0.010	18.2	29.3	1.71	0.05
7	0.39	2.48	0.94	0.019	0.010	18.2	29.2	1.66	0.68
8	0.30	1.62	0.92	0.017	0.009	17.5	29.3	1.75	0.83

scrap, nickel, and ferrochromium. After melting, the technically pure chromium (Cr99) was added, and the melt temperature was raised to 1600 ÷ 1650 °C. After holding the metal at this temperature for 5 minutes, ferrosilicon and ferro-manganese were added, and the melt temperature was raised up to 1700 °C (the temperature was monitored by an immersed PtRh10-Pt thermocouple).

The next step included deslagging and deoxidising of metal by means of aluminium added in an amount of 0.05 %. After this operation, the preheated ferroniobium and ferrotitanium, disintegrated to the size of 10 – 30 mm, were introduced in batches to the melt surface. When the ferroalloys melted down completely, the metal was tapped to 50 kg capacity ladles preheated at a temperature of 600 °C, and moulds were poured. The metal temperature on pouring was 1470 ± 25 °C. The chemical composition of the melts is given in Table 3.

To examine the alloy macro- and microstructure, bars of Ø20×70 mm were cast in open moulds made from the chemosetting sand mixture.

### 3. DISCUSSION OF RESULTS

Comparing the data compiled in Tables 1 and 3, and by reference to the assumptions made previously in calculation of the charge burden, it can be stated that during melting there were changes in the chemical composition of alloy consistent with what had been expected previously. The only exception was silicon content in melt and titanium melting loss; in both those cases the increase of the content considerably exceeded the values anticipated previously.

**Carbon.** The carbon content in individual melts was changing within quite a broad range of values. Never-

theless, as shown in Table 3, with exception of alloy No. 7, it has never gone beyond the anticipated range of 0.25 – 0.35 %.

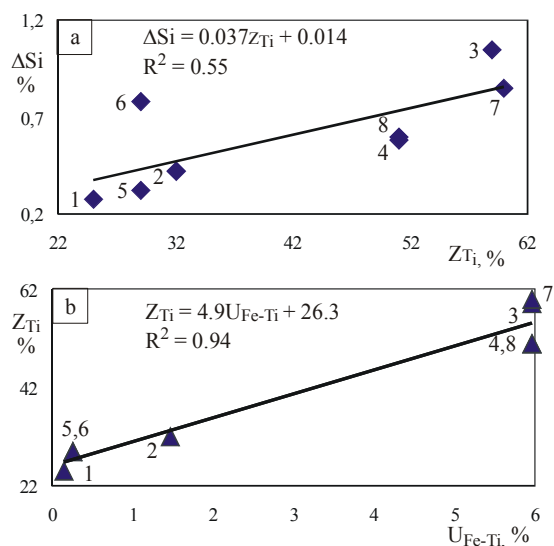
The starting content of carbon in charge materials should be 0.35 %, but it has been assumed that during melting it will get reduced according to equation (1), followed by a considerable increase of the silicon content in melt. This relationship did precisely exist in alloys No. 1, 4, 5, 6 and 8, while in the remaining alloys (alloys No. 2, 3 and 7) an increase in the silicon content was not accompanied by the expected drop of carbon content – Table 3. There are no grounds to judge that the course of physico-chemical reactions taking place in alloys from these two groups might be for any reason different. Therefore it should rather be assumed that after melting down, the content of carbon in alloys No. 2, 3 and 7 was much higher than the anticipated one.

The main source of carbon content in the charge was pig iron. Its 6 % content should have given about 0.26 % carbon in alloy. The remaining 0.09 % was supposed to come, first and foremost, from the steel scrap as well as from the ferrochromium and ferromanganese. So, if we assume that carbon content in the charge materials used for melts No. 2, 3 and 7 was too high, then the simplest explanation will be looking for a lack of homogeneity in the chemical composition of pig iron – in some pieces the carbon content might have been higher than that stated by the analysis. Yet, an explanation like this can hardly be considered sufficient and satisfactory, specially as regards melt No. 7 in which carbon content is so high that it cannot be justified even by an effect of other additional factors, like an elevated content of pig iron in the charge.

**Silicon and titanium.** As expected, obtaining the anticipated content of both elements has proved to be the task most difficult in the case of high-alloyed cast steel melted in an acid-lined induction furnace. From a comparison of the silicon content levels assumed in the charge (Table 1, item B) and obtained in reality (the values compiled in Table 3), it follows that the assumption of having a mean increase of silicon content in the melt by a value of 0.2 % has never been achieved in any of the eight melts. In reality, this increase was comprised in a range from 0.28 to 1.05 %. A similar unstable behaviour was observed in the case of titanium, too. The true titanium melting loss was from 25 to 60 % (see Tables 1 and 3). Irrespective of this, the mean titanium melting loss calculated for all the melts amounted to about 45 %, and in this approach it is consistent with the value adopted in theory. Obviously, the great divergences in the values of titanium loss are not a surprise. In the case of cast steel melted in an acid-lined furnace, the titanium melting loss may reach even 100 % [2].

The rate of the reaction proceeding according to equations (1) and (2) is a function of the temperature and time of liquid metal holding [4]. In the case under discussion, the time interval required for the ferroalloys to dissolve at a temperature of 1700 °C has proved to be the factor most critical in maintaining the previously anticipated content of silicon and titanium. Assuming that at that stage of the melting process the temperature of the melt was relatively stable, it must have been the time of the liquid metal holding that decided about the

metal/refractory reaction. The time of holding was the longer, the higher was the addition of ferroalloys to the alloy. A consequence of this assumption should have been the existence of two relationships: a relationship between the increase of silicon content in melt and the amount of added ferroalloys, and a relationship between the titanium melting loss and the content of ferrotitanium in charge. Using a Statistica 5.1 programme it has been checked if there is any relationship between the total content of ferrotitanium and ferroniobium in charge and the silicon content increase in melt. The calculations have not confirmed a validity of this assumption. On the other hand it can be proved that an increase in the silicon content is related with the value of titanium melting loss and the addition of ferrotitanium (Fig. 1). The lack of any relationship in the case of the total amount of the added ferroalloys, and the existence of such relationship in the case of a sole addition of ferrotitanium (1) can be explained by differences in the properties of both ferroalloys. The low, in respect of ferroniobium, density of ferrotitanium (about 6.2 g/cm<sup>3</sup> [9]) makes it rest on the surface of melt while dissolving. Additionally, the high (in alloys No. 3, 4, 7 and 8) six percent content of ferrotitanium in charge forces it to be introduced to the melt surface in batches to avoid “freezing” of the furnace crown (the crucible diameter in an IMSK 100 furnace is small and amounts to about 230 mm). The amount of ferroniobium is definitely much smaller (see Table 2), and owing to its high density it immerses in metal quite easily. Therefore, compared to ferrotitanium, its effect on the total time required by ferroalloys to get dissolved is of minor importance.



**Fig. 1.** The results of measurements: a – effect of titanium melting loss ( $Z_{Ti}$ ) on increase of silicon content in melt ( $\Delta Si$ ); b – effect of ferrotitanium content in charge ( $U_{Fe-Ti}$ ) on titanium melting loss ( $Z_{Ti}$ )

Fig. 1, a, specifies for each alloy the values of the titanium melting loss ( $Z_{Ti}$ ) and the corresponding values of the silicon content in melt ( $\Delta Si$ ). The plotted line of trend is, however, characterised by low statistical parameters. The alloy responsible for this fact is, first of all, alloy No. 6. In spite of the low total content of the stabilisers, it

is characterised by a high value of ( $\Delta Si$ ). Following the assumptions adopted previously, this fact can be explained by a long time during which the melt was held at a temperature of 1700 °C.

It should be emphasized here that in practice high increase of the silicon content (of course, when kept under control) need not have an adverse effect on the quality of the creep-resistant cast steel. These cast steels usually contain silicon in a range of 1 to 2.5 % Si (see DIN 17465 - Hitzebeständiger Stahlguß [10]).

Introducing more titanium is also related with heavy destruction of the furnace refractory lining. In the case under discussion, in melts No. 3, 4, 7 and 8, the refractory lining was capable of withstanding three melts maximum.

**Niobium.** As shown in Tables 1 and 3, the adopted assumption of a “zero” melting loss of niobium has been entirely false. From a comparison of the anticipated and true content levels of this element in alloys it clearly follows that the melting loss of niobium was comprised in a range of 4 – 9 %, and this value was increased with increasing addition of ferroniobium.

It was expected that the applied ferroniobium with 1.2 % silicon would be, because of its high density (about 8.4 g/cm<sup>3</sup> [9]), “sucked in” under the melt surface quite easily. As a consequence, the melting loss of niobium should be minimal. The role of the ferroniobium density in its easy and effective penetration inside the melt has been indirectly indicated by the results of a research described in [11]. In the melts in which ferroniobium (11 – 24 % Si) and siliconiobium (20 – 42 % Si), and hence the two master alloys of a density much lower than the density of the alloys described in this study, were used, the melting loss of niobium was comprised in a range of 10 to 50 %.

On the other hand, it can be expected that the rate of the niobium melting loss could be smaller, if ferroniobium had been introduced as a separate addition before introducing ferrotitanium to the melt surface.

**Manganese.** With the content of about 1 % manganese in the charge, it was expected that its final content in alloys would be oscillating somewhere around the value of 0.8 %, whereas, as shown in Table 3, its average content was 0.95 %. So, in practice, the true relative melting loss of this element was from 3 to 9 % and was, on an average, three times smaller than the value anticipated previously.

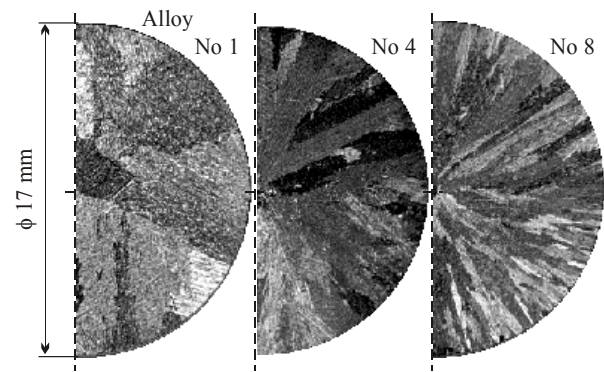
**Chromium.** In all melts the melting loss of chromium was as expected and comprised in a range of 8 to 12 %.

**Nickel.** In all melts the melting loss of this element was up to 3 %. Hence it follows that, when calculating the charge burden for melting the creep-resistant cast steel, one can without any greater risk assume a “zero” melting loss of nickel, providing its content in the charge is equal to a mean value recommended by, e.g., the above mentioned standard - DIN 17465.

The results discussed here prove that melting in an acid-lined induction furnace of nickel-chromium cast steel containing titanium as an alloying element is the task very difficult. Therefore, the relationships presented in Fig. 1 may prove to be quite useful when melts similar to the ones described in the present study are designed. It is also necessary to remember that when small-capacity furnaces are used, the effect of an incidental heterogeneity in single

pieces of the charge on final output of the melting process becomes much more serious. In this context, careful control of homogeneity of the chemical composition, of the presence of impurities (slag, for example), and of the charge burden to be weighed very precisely, is a must in correct industrial practice.

As a consequence of the presence of varied amounts of the stabilising elements in alloys, a significant difference in their as-cast structures should be expected. In the case under discussion, this difference is visible in both macro- and microstructures shown in Fig. 2 and Fig. 3. In as-cast condition, the alloy structure is composed of the co-existing austenitic matrix and primary carbide precipitates present in the interdendritic spaces and, though more rarely, on the grain boundaries (Figure 3). Basing on an analysis of the structure images it can be observed that increasing the niobium and/or titanium content in alloy reduces the size of the grains and dendrites as well as the degree of refinement of the primary carbide phases. So, these are the changes typical also of an inoculation effect. On the other hand, all alloys have preserved their trans-crystalline structure with columnar arrangement of crystals (Fig. 2).



**Fig. 2.** Examples of macrostructures. Etched at a temperature of 50 °C with reagent of the following composition: 10 ml HNO<sub>3</sub>, 20 ml HCl and 30 ml of glycerin

To assess quantitatively the grain refinement in structure caused by an addition of the stabilising elements, the spacing between the secondary dendrite arms was measured. The mean values ( $d$ ) from the ten measurements taken for every alloy are compiled in Table 4.

**Table 4.** Mean values ( $d$ ) of spacing between the secondary dendrite arms

Alloy	1	2	3	4	5	6	7	8
$d, \mu\text{m}$	51.2	41.5	36.7	34.4	33.7	31.4	26.8	27.7

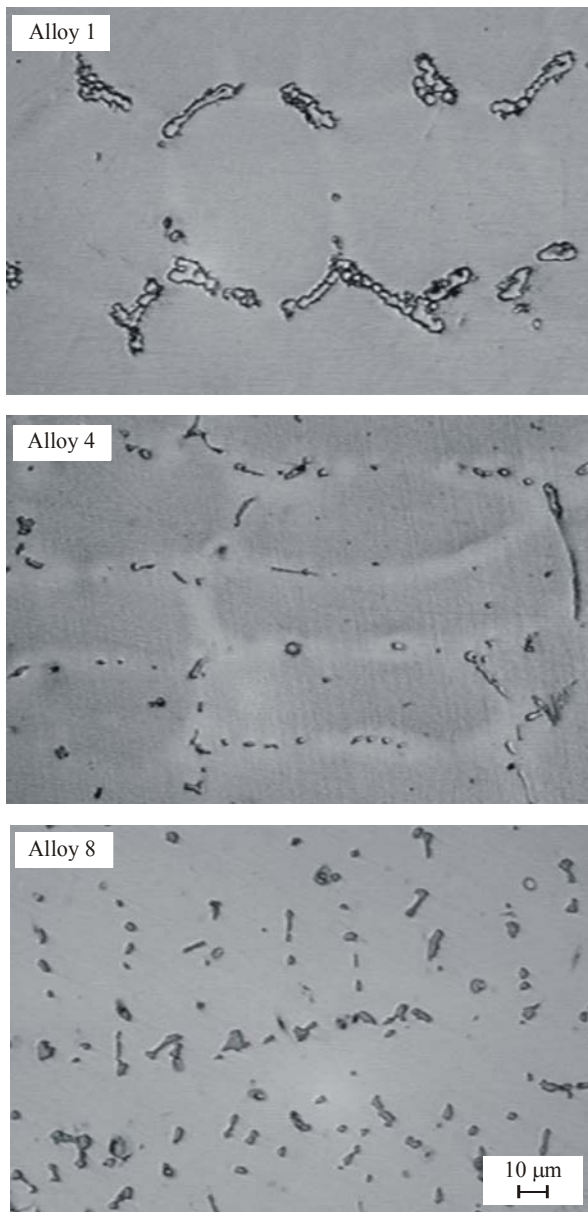
Using a Statistica 5.1 program, a relationship between the value  $d$  and the content of niobium and titanium in alloy was determined:

$$d = 51.7 - 11.2 \times (\%Nb) - 18.3 \times (\%Ti) + 6.7 \times (\%Nb \times \%Ti) \quad (3)$$

for the value of the coefficient of determination  $R^2 = 0.98$  and F-Snedecor test  $F = 68.4$ .

From equation (3) it follows that increasing the content of niobium and/or titanium in alloy reduces the value of  $d$ , the combined effect of both these elements

being much more prominent. At the same time, titanium exerts stronger effect than niobium on a value of this structure parameter. For example, equation (3) assumes the value of  $d = 35 \mu\text{m}$  for about 0.9 % titanium or 1.4 % niobium.



**Fig. 3.** Examples of microstructures; etched with reagent of the following composition: 10 g  $\text{K}_3\text{Fe}(\text{CN})_6$ , 10 g KOH and 100 ml  $\text{C}_2\text{H}_5\text{OH}$

#### 4. CONCLUSIONS

1. When melting austenitic 0.3 % C – 30 % Ni – 18 % Cr cast steel stabilised with niobium and/or titanium in an acid-lined induction furnace of small capacity, the following relative values of melting loss (–), or increase (+) in the content of its constituents were recorded:

Si	Mn	Cr
+ (16 – 100) %	– (3 – 9) %	– (8 – 12) %
Ni	Nb	Ti
max. (– 3 %)	– (4 – 9) %	– (25 – 60) %

2. The increase in niobium and/or titanium content in alloy from 0.03 % up to 1.8 % Nb and 1 % Ti, respectively, was not observed to eliminate the presence of transcryalline structure in thin-walled castings, but it caused the grain refinement. The grain refinement seemed to have been achieved more easily with increased content of titanium in alloy rather than with that of niobium.

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