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ALUMOTHERMIC REDUCTION OF ILMENITE IN A STEEL MELT

ALUMOTERMIČNA REDUKCIJA ILMENITA V JEKLENI TALINI

Jaka Burja[1], Franc Tehovnik[1], Jakob Lamut[2], Matjaž Knap[2]

[1] Institute of Metals and Technology, Lepi pot 11, 1000 Ljubljana, Slovenia
[2] University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Materials and Metallurgy, Aškerčeva 12, 1000 Ljubljana, Slovenia
jaka.burja@imt.si

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Experiments regarding the alumothermic reduction of ilmenite ($FeO{\cdot}TiO_2$), a mineral that contains iron and titanium oxides, were carried out. The results of the experiments showed that the alumothermic reduction takes place in steel, but the products obtained with the reduction suggest that the reaction mechanism is more complicated and includes different metallic phases other than a simple reduction of pure elemental titanium. Two kinds of experiments were carried out, the alumothermic reduction of ilmenite in a steel melt and the alloying of the alumothermic mixture into the steel melt. The experiments were carried out in order to get a view of the phase boundary between the steel and reduced titanium and the metallic phases that occur during the reduction, before the dissolution of titanium in the steel melt. Metallic phases that contained aluminium, iron and titanium were gained during the alumothermic reduction of ilmenite. Titanium was successfully alloyed into the steel melt by introducing the alumothermic mixture into the melt, while the presence of titanium nitrides confirms that the titanium was reduced in the melt and reacted with the dissolved nitrogen.

Keywords: alloying of titanium, ilmenite, alumothermic reduction, titanium in steel

Izvedeni so bili poskusi alumotermične redukcije ilmenita. Ilmenit je mineral, ki vsebuje titanove in železove okside ($FeO{\cdot}TiO_2$). Rezultati so potrdili, da v jeklu poteče alumotermična redukcija. Produkti redukcije pa kažejo na to, da je reakcijski mehanizem bolj zapleten, kot pa zgolj nastajanje elementarnega titana, saj nastajajo različne kovinske faze. Izvedeni sta bili dve vrsti poskusov: alumotermična redukcija ilmenita in legiranje alumotermične mešanice v jekleno talino. Dobljen je bil vpogled v procese na fazni meji med jekleno talino, titanom in nastalimi kovinskimi fazami, preden se titan raztopi v jeklu. Ugotovljeno je bilo, da se titan raztaplja v jeklu prek nastanka intermetalnih faz. Produkti redukcije so bile kovinske faze, ki so vsebovale aluminij, titan in železo. Prisotnost titanovih nitridov v jeklu, ki smo ga legirali z mešanico, pa je dokaz, da je bil titan legiran v kovinski obliki, kjer je reagiral z raztopljenim dušikom.

Ključne besede: legiranje titana, ilmenit, alumotermična redukcija, titan v jeklu

1 INTRODUCTION

Titanium is an important alloying element in steel making, among other things, it is used to stabilise stainless steel by forming titanium carbides and preventing the formation of chromium carbides. It has also been observed that additions of titanium significantly reduce the austenite grain size in the as-cast microstructure of continually cast steels.[1] Titanium's high chemical affinity to nitrogen and carbon is what makes it such a valuable alloying element, but unfortunately it also makes it difficult to alloy (low yields) and produce.[2] The production of titanium is complex and therefore expensive.[3] In steelmaking titanium is used in the form of ferrotitanium that contains iron and between 20 to 75 % of titanium, while its eutectic composition is at the mole fraction 71.1 % of Ti.[4,5] Ferrotitanium is mostly produced by remelting titanium scrap and iron; the high prices of titanium consequently mean that the price of ferrotitanium is also relatively high. Experiments that concern direct alloying of titanium from the oxide form may show an alternative way of producing ferrotitanium, as the minerals like ilmenite that contain titanium oxides are inexpensive. Alumothermic reduction was chosen because aluminium is often added to ferrotitanium in order to increase the yield by reducing the oxidised titanium in a steel melt.[6]

The Ellingham diagram (**Figure 1**) clearly shows that the Gibbs free energy for the alumothermic reduction of titanium is negative. The alumothermic reduction of titanium in the oxide form is as follows:

$$3TiO_2 + 4Al = 3Ti + 2Al_2O_3$$

The alumothermic reduction of ilmenite has an even lower Gibbs free energy because ilmenite contains iron oxides and its equation is as follows:

$$FeO{\cdot}TiO_2 + 2Al = Fe + Ti + Al_2O_3$$

As we can see from reaction (2) iron is another metal product besides titanium. The graph for the value of the Gibbs free energy for equations 1 and 2 is given in **Figure 2**[7].

Titanium forms TiO_2 if oxygen is present in the steel melt, while titanium oxide forms high temperature phases with other oxide components in the slag. If CaO is present perovskite $CaO{\cdot}TiO_2$ forms with its melting point at around 2000 °C. Titanium oxide particles can also get trapped in spinel $Al_2O_3{\cdot}MgO$, which can also

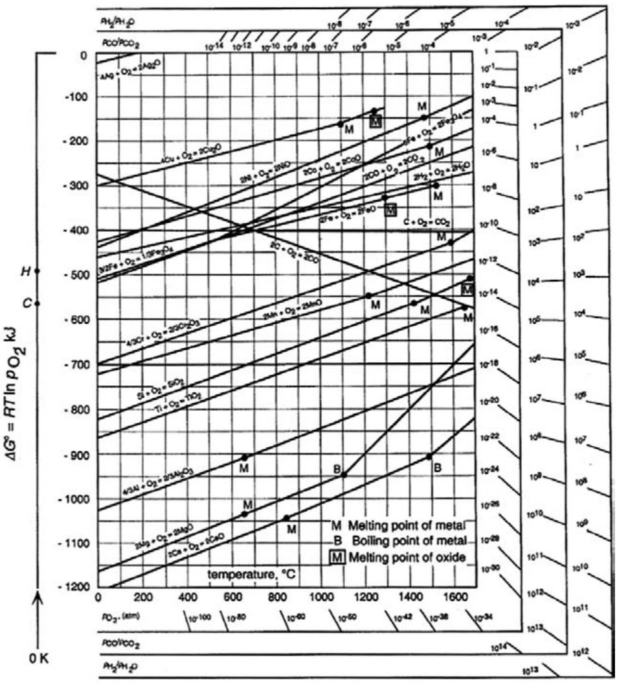

Figure 1: Ellingham-Richardson diagram
Slika 1: Ellingham-Richardsonov diagram

present a problem, because a spinel melts at the temperatures higher than 1600 °C and the titanium oxide particles have a melting point at around 1800 °C.[8] The formation of non-metallic inclusions that have a high melting point is problematic with respect to the cleanliness of steel and is therefore undesirable. The control of oxide non-metallic inclusions can be achieved by lowering the aluminium content and, therefore, the Al_2O_3 content and by decreasing the MgO content in the rafination slag.[8] The $CaO{\cdot}TiO_2$ content is lowered by lowering the basicity of the slag (CaO/SiO_2).[8]

In the production of stainless steel, a strong nitride-forming element, such as titanium, is often added to stabilise nitrogen and improve the mechanical properties of steel via the grain refinement during hot rolling. On the other hand, titanium nitride formed in liquid steel can agglomerate and cause a nozzle-clogging problem during continuous casting, and surface defects in the final products.[9] In practice the deposit material that is clogging the nozzle is titanium oxide and spinel, but research work has shown that the agglomerates form because titanium nitride particles get caught in the spinel; these are in turn oxidised and become titanium oxides. The particles remain rectangular like nitrides and not globular like oxides formed in the melt. The presence of oxygen is probably the result of porosity of the refractory material, from which the nozzles are made. The flow of the metal trough the nozzle creates a low pressure, which, in turn, promotes the diffusion of oxygen trough the pores into the melt.[10]

The experiments were carried out taking into account the specific nature of titanium and its behaviour as an alloying element.

2 EXPERIMENTS

The experiments were carried out using steel pipes filled with an alumothermic mixture of aluminium and ilmenite. These pipes were then introduced into the steel melt where the mixture was heated up to approximately the temperature of the steel melt. The mixture reacted at such high temperatures. In one set of the experiments the pipes were retrieved before they fully dissolved and still contained the mixture, which had been sintered by the high temperatures. The other set of experiments had been designed to alloy titanium into the steel and in this case the pipes were fully dissolved, together with the mixture. This procedure was carried out in order to recreate the conditions of alloying with the use of a cored wire.

The alumothermic mixture consisted of the ilmenite dust and aluminium dust. The molar ratio was 1 : 4 for ilmenite to aluminium, and the surplus of aluminium was

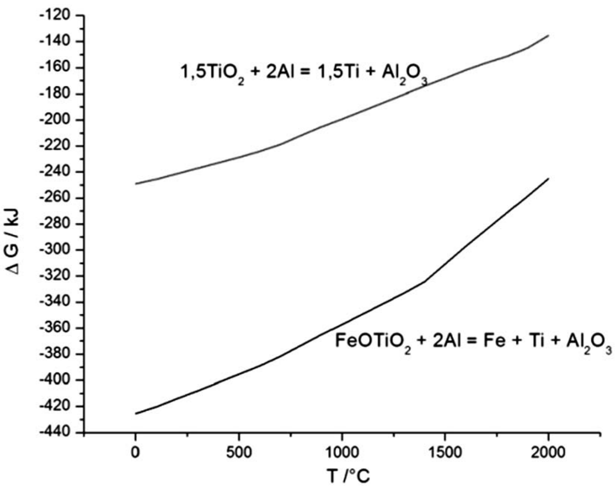

Figure 2: Gibbs free energy for equation 2[7]
Slika 2: Gibbsova prosta energija za reakcijo 2[7]

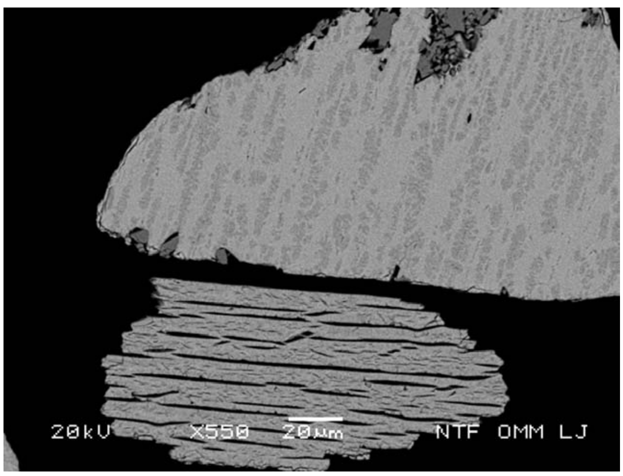

Figure 3: Ilmenite grains
Slika 3: Ilmenitna zrna

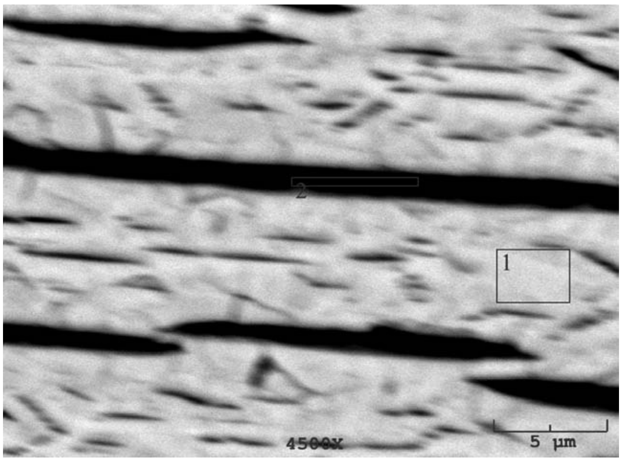

Figure 4: Phase analysis of ilmenite
Slika 4: Fazna analiza ilmenita

used so that the reduction took place. Theoretically, a molar ratio of 1 : 2 is needed to reduce ilmenite, as can be seen from equation 2.

Ilmenite is a mineral that mainly consists of iron and titanium oxides in the form of $FeO \cdot TiO_2$, but it also contains impurities such as magnesium oxides and manganese oxides. SEM analyses show that grains of ilmenite are far from being homogenous but have a "striped" appearance that can be seen in **Figure 3**.

The phase analysis in **Figure 4** clearly shows that the darker stripes are richer in titanium, while the lighter ones are richer in iron.

An electric induction furnace with a capacity to melt 18 kg of steel was used to melt the steel for the experiments.

A steel melt was prepared for the experiments that were developed to model the alumothermic reduction of ilmenite. The steel melt was heated to the temperature of 1500 °C, measured with an optical pyrometer. The chemical composition of the steel melt is not important for the experiment because the steel melt is only used as a medium to transfer heat to the alumothermic mixture, not to interact with it chemically. Then the pipe with the alumothermic mixture was submerged into the melt for approximately 40 s. The pipe was 25.4 mm in diameter and had a wall thickness of 2 mm. This method was chosen because it was essential that the mixture was quickly heated up to the temperature of the steel melt in order to prevent the aluminium dust from oxidising and thus losing its ability to reduce ilmenite.

Another experiment was made in order to determine whether titanium can be alloyed into the steel melt with the alumothermic ilmenite reduction. The aim was to alloy the mass fraction 0.3 % of titanium into 18 kg of steel. The required amount of ilmenite was 171 g and the amount of aluminium was 121 g.

First the steel was melted; it had a small quantity of alloying elements and a deep drawing quality. When the steel was melted a sample was taken for a chemical analysis. It was found that it did not contain detectable levels of titanium (the method of determining the titanium content was the classical chemical analysis). Then the melt was deoxidised with aluminium, after that the steel pipes were filled with the alumothermic mixture and submerged into the melt until they dissolved, thus, alloying the steel with titanium when the pyrometer gave a temperature reading of 1600 °C.

A sample of the alloyed steel was taken after the alloying was complete; the rest of the steel was cast into an ingot. Samples of slag were taken as well.

3 RESULTS

The steel pipes that were used for the reduction of ilmenite were partially melted, but there was a sintered mass in the pipe. Metallographic samples were made and a further SEM analysis showed that metallic phases containing aluminium, iron and titanium were present. **Figure 5** shows the products of the alumothermic reaction; metallic phases contain aluminium, iron and, most importantly, titanium.

Figure 6 shows a part of the sintered mass in the steel pipe after the reduction; individual intermetallic phases can be seen. The metallic phases are surrounded by the oxide products of the reduction.

The chemical compositions of the phases from **Figure 6** are given in **Table 1**.

In the experiment that investigated the option of alloying titanium, the mixture had reacted and the

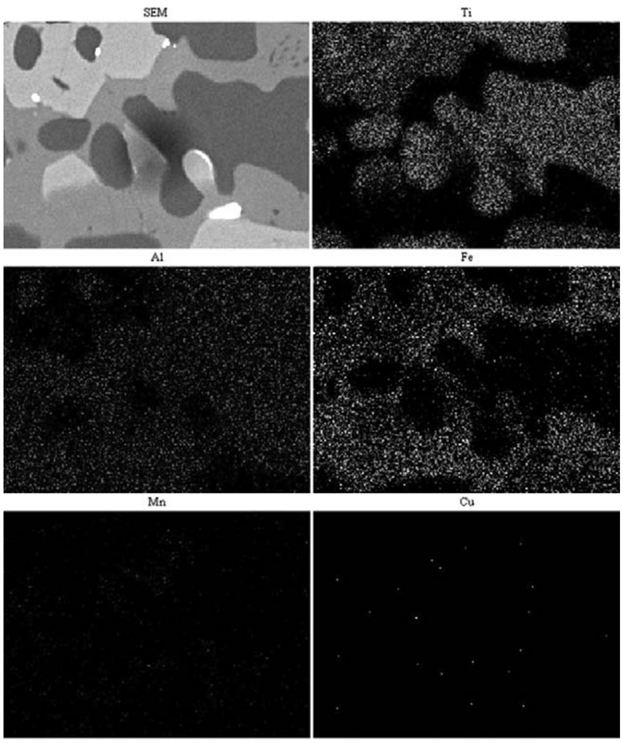

Figure 5: Mapping of alumothermic products
Slika 5: Ploskovna porazdelitev elementov redukcijskih produktov

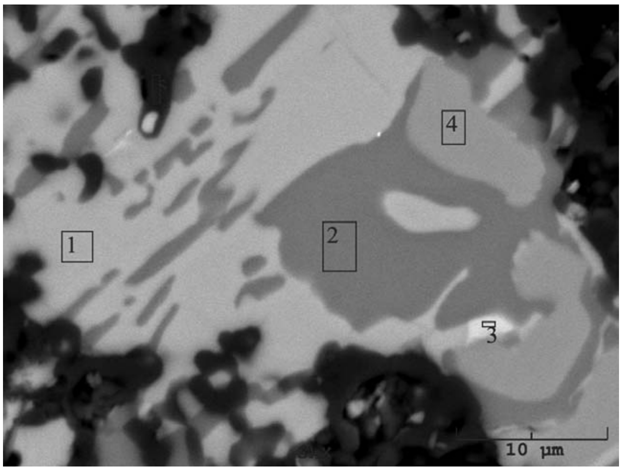

Figure 6: SEM image of the products of the alumothermic reduction
Slika 6: SEM-posnetek produktov alumotermične redukcije ilmenita

Table 1: Chemical compositions of the phases (in mass fractions *w*/%) from **Figure 6**
Tabela 1: Sestava faz (v masnih deležih *w*/%) s **slike 6**

1	48.4 % Al	6.0 % Ti	43.4 % Fe	1.3 % Cu		0.9 % Mn
2	52.2 % Al	45.5 % Ti	1.6 % Fe		0.7 % Si	
3	33.5 % Al	30.0 % Ti	28.7 % Fe	1.6 % Cu	5.4 % Si	0.8 % Mn
4	44.5 % Al	42.7 % Ti	12.8 % Fe			

product or the alumothermic reduction began to dissolve into the steel melt. The presence of titanium nitrides in the microstructure, as seen in **Figure 7**, confirms that titanium had indeed been alloyed into the steel and had reacted with the nitrogen in the steel melt. The chemical analysis showed that the content of titanium had been raised up to $w = 0.064$ %. The yield of titanium can be calculated with equation 2 and is therefore 21 %.

$$Yield = 0.064/0.3 \times 100\ \% = 21\ \%$$

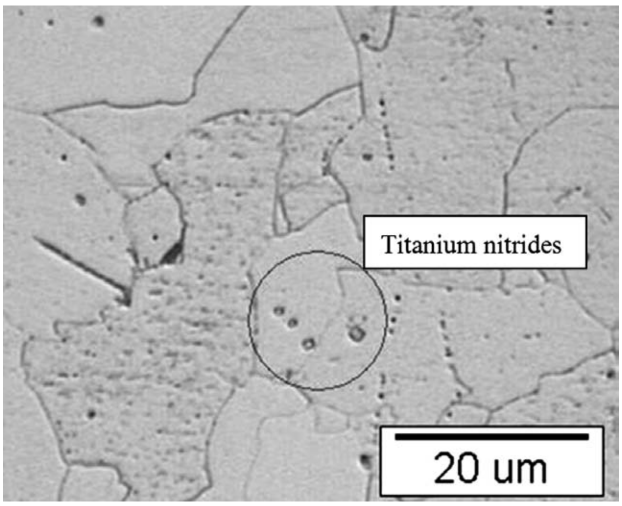

Figure 7: Titanium nitrides in the steel microstructure
Slika 7: Titanovi nitridi v mikrostrukturi jekla

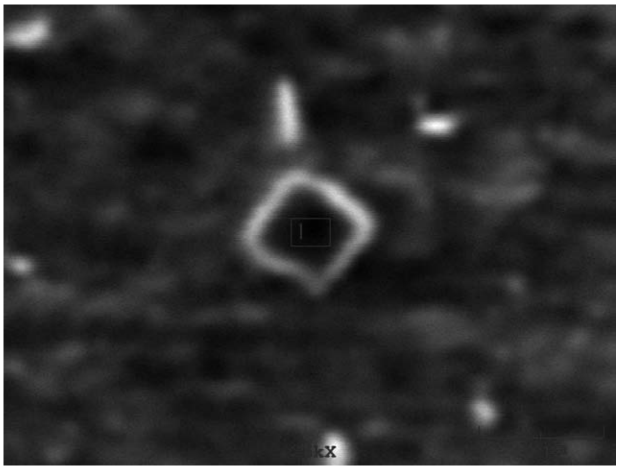

Figure 8: SEM image of a titanium nitride
Slika 8: SEM-posnetek titanovega nitrida

Figure 8 shows the SEM analysis of the nitrides confirming that the inclusions in **Figure 7** were indeed titanium nitrides.

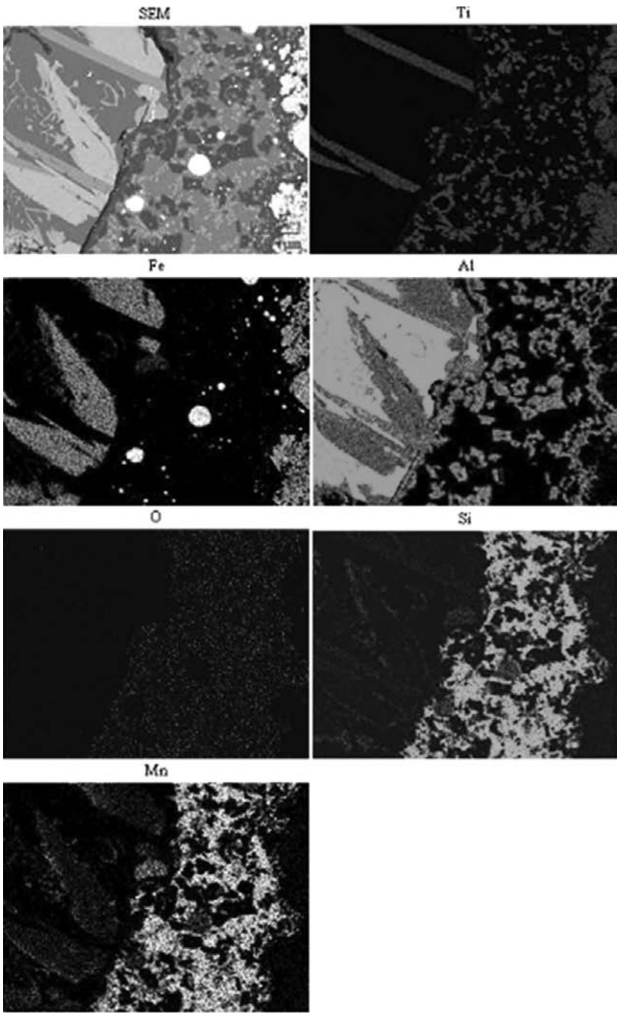

Figure 9: Mapping of the slag
Slika 9: Ploskovna porazdelitev elementov v žlindri

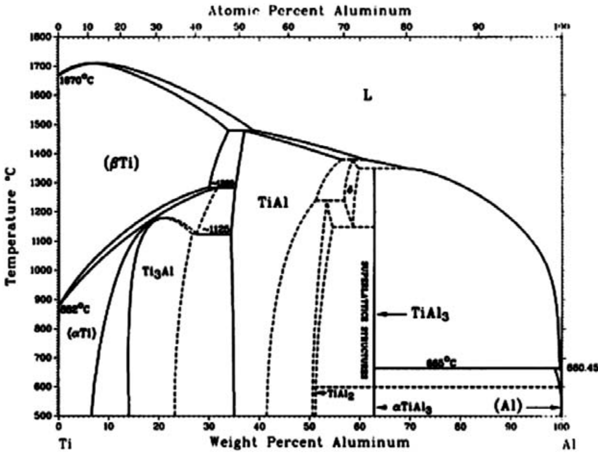

Figure 10: Ti-Al binary phase diagram[12]
Slika 10: Binarni fazni diagram Ti – Al[12]

Next the slag was analysed in order to further widen the understanding of the processes that took place during alloying. An interesting discovery was made during the analysis of the slag: a relatively large content of metallic phases.

The content of the elements is clearly shown in **Figure 9**, where the metallic parts in the slag are mostly aluminium, but the most important factor is that the metallic parts contain reduced titanium and that can be directly linked to a lower yield. There is also a significant amount of titanium in the oxide part of the slag as shown in **Figure 9**. A part of the alloying mixture had clearly floated onto the surface and got entrapped in the slag.

4 DISCUSSION

Alloying titanium into the steel melt by alumothermicaly reducing ilmenite can be divided into several stages: heating up the alumothermic mixture, the alumothermic reaction, the formation of alloys and intermetallic phases of iron, titanium and aluminium, the dissolution of the intermetallic phases and, therefore, titanium into the steel melt, and the reaction between titanium and nitrogen in the steel melt. The first part of the experiments showed us that elemental titanium does not form, instead intermetallic phases are formed and they consist mostly of aluminium. These results can be compared with those of N.J. Welham and associates, considering that the surplus of aluminium they used was significantly higher.[11] Possible future work should consider that aluminium is not needed just for the reduction, but for forming the alloys with titanium. The phase that contained the highest amount of titanium, 45.5 %, the phase number 2 from **Table 1**, was based on aluminium. It is clear that the tendency of titanium to form intermetallic phases with aluminium is higher than that to form them with iron. It can be speculated, from the phase diagram Ti–Al (**Figure 10**), that Al_3Ti with 63 % Al and 27 % Ti forms during the alumothermic reduction.[12] But in the cases that have a lower surplus of aluminium, AlTi should form, as can be seen from the Ti–Al phase diagram.

The experiments that dealt with the alloying of titanium into the steel melt show us quite a different problem than that of getting the right molar ratio of the ingredients for the reduction: the problem of a lower density and, therefore, buoyancy. A large part of the titanium that was reduced in the melt ended up in the slag due to its floating onto the surface of the melt and into the slag. The products of the alumothermic reduction were found in the slag together with aluminium. The metallic phases, especially aluminium, in the slag indicate that not only did some products of the reduction get entrapped in the slag, but aluminium and unreduced ilmenite did as well and the reduction also took place in the slag. The other part of the titanium was alloyed into the melt and formed nitride inclusions in the steel melt. A part of the alumothermic products clearly had time to dissolve in the melt.

A study of the thermodynamic stability of the intermetallic phases of aluminium and titanium and their effect on the thermodynamics and kinetics of the reduction should be made and their ability to dissolve in liquid steel should be observed. Further experiments with cored-wire injections should be studied. The effect of such alloying on the number and size of non-metallic inclusions should be studied as well.

5 CONCLUSIONS

Titanium can be alloyed into the steel melt by alumothermicaly reducing ilmenite.

Intermetallic phases of titanium and aluminium, not elemental titanium, form during the reduction.

The forming of intermetallic phases of titanium and aluminium requires an even higher surplus of aluminium.

The low density of the ingredients for the alumothermic reduction and the products further decreases the yield.

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