Vacuum Induction Melting – Optimisation of Pressure Dependent Reactions

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Abstract

The VIDP (Vacuum Induction Degassing and Pouring) is the most important melting plant in the production of high-purity steels for aircraft and aerospace industry. Those material grades are featured by a very low level of trace elements such as oxygen, nitrogen and in many cases carbon. During vacuum melting pressure dependent reactions like nitrogen removal, vacuum-decarburisation and vacuum-deoxidation can proceed and control the content of those trace elements. But thermodynamic equilibrium can't be reached in VIDP operating range of a pressure of approximately 10^{-5} bar in economical reasonable time. Interface phenomena's inhibit the formation of reaction products and slow down the reduction of trace elements noticeably. These are amongst others the energy to form bubbles below the liquid metal surface or the interface allocation by surface active elements such as sulphur, which are reported in literature.

The aim of this project is to evaluate the "process-equilibria" of pressure depending reactions for different steel grades and to determine optimisation potential in lowering the content of trace elements. Investigations and experiments were carried out at alloys with different carbon levels and compared with literature and theory. The degradation of carbon, oxygen and nitrogen against time could be displayed by special sampling at the beginning of the melting and vacuum treatment. Thermodynamic calculations were worked out to evaluate the theoretical, pressure depending limits. In reality quasi-stationary conditions, which were not in thermodynamic equilibria, occurred for each alloy composition. Anyway, literature data showed that the VIDP can reach lower content of C, O and N in comparison to other vacuum plants by its characteristic melt agitation.

Keywords: VIDP, Vacuum Metallurgy, Decarburisation, Deoxidation, Removal of Nitrogen, Refining

Introduction

Special steels for aircraft applications require high demand on the production process. Vacuum metallurgy, melting by VIDP (Vacuum Induction Melting Degassing and Pouring) and remelting by VAR (Vacuum Arc Remelting), is indispensable manufacturing such alloys to improve mechanical properties such as durability, heat- and corrosion resistance or weldability. Vacuum metallurgy is used to achieve following objectives:

- Removal of dissolved gases

- Removal of undesired trace elements with higher vapour pressure

- Prevention of oxidation reactions due to air contamination resulting in minor losses of reactive elements

- Control of pressure dependent reactions such as decarburization

- Highest cleanliness

- Achievement of very closely compositional tolerances

To obtain lowest oxygen and/or carbon contents vacuum deoxidation/decarburisation is the reaction of particular importance during VIDP refining. Vacuum deoxidation can reach a very high deoxidation potential due to the pressure dependence of the C-O-reaction. The reaction product is gaseous and can be removed without the formation of non-metallic inclusions [1].

This paper discusses the metallurgical reactions during the refining period of the VIDP furnace such as vacuum decarburisation/deoxidation and removal of nitrogen as well as their limitations.

Vacuum Metallurgy

Slag/Metal Reactions

The usage of slag in vacuum induction furnaces is limited. The geometry of common induction furnaces is disadvantageous due to the low ratio of crucible diameter to crucible height. Furthermore the typical bath agitation pushes the slag to the crucible wall where heavy attack to the refractory lining occurs and reactions between metal and slag, e. g. desulphurisation, are restrained. To achieve lowest sulphur contents, desulphurisation agents like Ca or Mg are in use [2].

Evaporation Reactions

Trace elements like Te, Pb, Se or Bi fortunately can be removed due to their high vapour pressure by vacuum metallurgy. The VIDP furnace represents an excellent melting unit where pressures of 10^{-2} mbar and lower can be reached [3].

Gas Reactions

The solubility of gases depends on pressure, temperature, and chemical composition. Temperature and chemical composition are predetermined in the majority of cases. Vacuum treatment by VIDP allows to reduce the pressure about orders of magnitude and

ensures the reduction of dissolved gases like nitrogen according to Sieverts's law.

$$[N] \leftrightarrow \tfrac{1}{2}\{N_2\}$$

$$K_N = \frac{\sqrt{p_{N_2}}}{a_{[N]}}$$
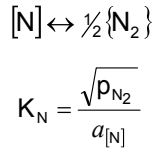
Unfortunately, the reaction shown above can be inhibited by surface active elements like O and S and can take a long time to reach equilibrium at very low pressures due to kinetic limits. CO-boiling and stirring of the melt enhances the removal of nitrogen [4].

Deoxidation/Decarburisation Via Gas Phase

Deoxidation or decarburisation takes place through the formation of carbon monoxide according to the following equation:

$$[C] + [O] \leftrightarrow \{CO\}$$
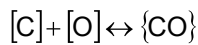
As the reaction product is gaseous, the oxygen-content is directly proportional to the CO-partial pressure p_{CO}.

$$K_{CO} = \frac{p_{CO}}{a_{[C]} \cdot a_{[O]}}$$

Reduced pressure by vacuum treatment allows to reach lowest C and O-contents without the formation of non-metallic inclusions. Figure 1 shows the theoretical equilibria of the C-O-reaction in dependence of the pressure [4, 5].
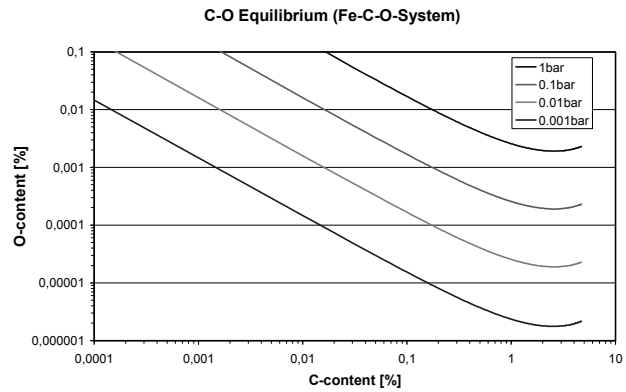

Figure 1: Theoretical C-O equilibrium of the Fe-C-O-system for various pressures and 1600°C

Investigations and Sampling

The investigations are carried out on a full-scale production plant, the VIDP furnace at the Böhler Special Steel Plant in Kapfenberg, Austria. The aim of this paper is a detailed description and understanding of metallurgical reactions during the refining period. Especially the removal of carbon, oxygen and nitrogen, the degradation rates and the "process-equilibria" at the end of the refining period are of interest. Therefore five different alloys with carbon contents in a range from 0.001% up to 0.8% are sampled in the earliest stage of melting, the refining period, in the VIDP furnace.

Alloy Concepts

The average chemical compositions of the test materials are shown in Table 1.

Table 1: Compositions of test materials

Material		Chemical composition (wt.%)									
Mat. No.	others	C	Si	Mn	Cr	Mo	V	Ni	Co	Ti	Al
1.6354	Marage 300	max. 0.03	-	-	-	5.00	-	18.50	9.00	0.70	0.10
1.6359	Marage 250	max. 0.03	-	-	-	4.90	-	18.00	8.00	0.55	0.13
1.4534	PH 13-8Mo	0.03	-	-	12.70	2.20	-	8.20	-	-	1.10
1.3590	M50 Nil	0.15	0.20	0.30	4,10	4.40	1.15	3.40	-	-	-
1.3551	M50	0.83	0.20	0.30	4.20	4.25	1.00	-	-	-	-

Table 2: Sample numbers

Sample.No	Ch.	P.1	P.2	P.3	P.4
Type	Calculated (charge)	Lollipop sample (charge molten)	Lollipop sample	Lollipop sample	Lollipop sample (End refining)

1.6354 and 1.6359 are ultra-high-strength maraging steels. In contrast to heat treatable steels their outstanding tensile properties are not achieved to a hardened structure with relatively high carbon content, but to precipitation of intermetallic phases from a ductile nickel bearing matrix containing almost no carbon.

1.4534 is a precipitation hardenable stainless steel with high stress corrosion resistance and high strength up to 315°C.

1.3551 (M50) material is a well-established through-hardening bearing steel and is the most commonly used material for main-shaft bearings. 1.3590 (M50NiL) material is the carburising version of 1.3551. 1.3590 has similar bearing properties to 1.3551 but higher fracture toughness in the uncarburised core.

In this paper, the investigations of 1.6359 – Marage 250 (lowest carbon content) and 1.3551 - M50 (high carbon content) are described in detail, whereas the others are summarised.

Sampling

Five chemical analyses during refining are carried out (see Table 2 for sample denotation). The first analyse "Ch." is calculated using the charging materials weight and composition. Samples P.1 to P.4 are lollipop samples taken from the liquid metal in the VIDP furnace at different times.

Results

Chemical Analysis and Degradation Rates

The behaviour of carbon, oxygen and nitrogen plotted against time is shown in Figure 2 for alloy 1.3551 (M50) and in Figure 3 for alloy 1.6359 (Marage 250). The carbon, oxygen and nitrogen contents are decreasing during the first stage of melting due to the low pressure and CO-boiling.
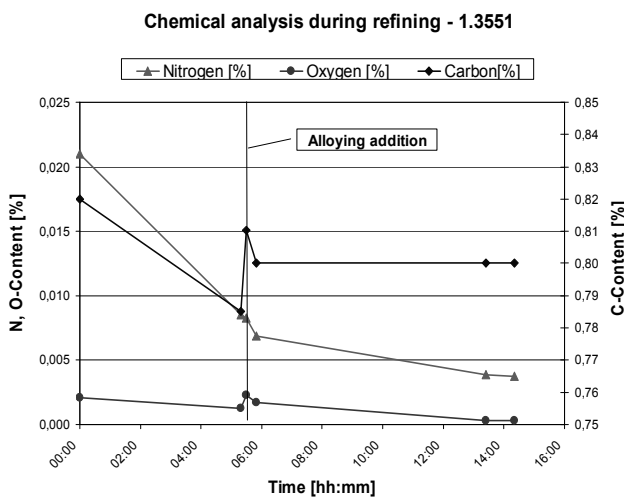

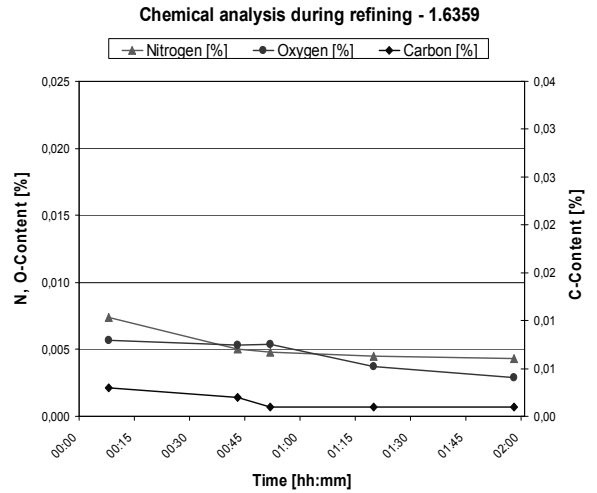Figure 2: Behaviour of C, O and N during refining of alloy 1.3551 (M50)

Figure 3: Behaviour of C, O and N during refining of alloy 1.6359 (Marage 250)

The decarburisation rate of the bearing steel is much higher than the rate of the maraging steel due to their completely different carbon contents (Figures 4 and 5). Furthermore alloying elements have been added between sample P.2 and P.3. Heavy boiling was monitored after alloying. The rate of nitrogen removal is high if the C-O reaction is in progress. Nitrogen removal continues at a very low but constant rate due to vacuum treatment even if decarburisation has already stopped.
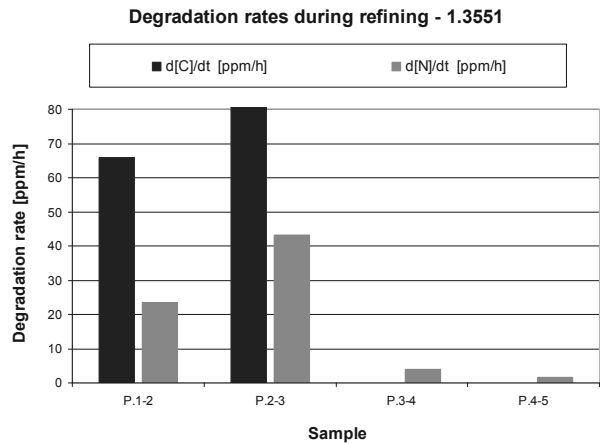

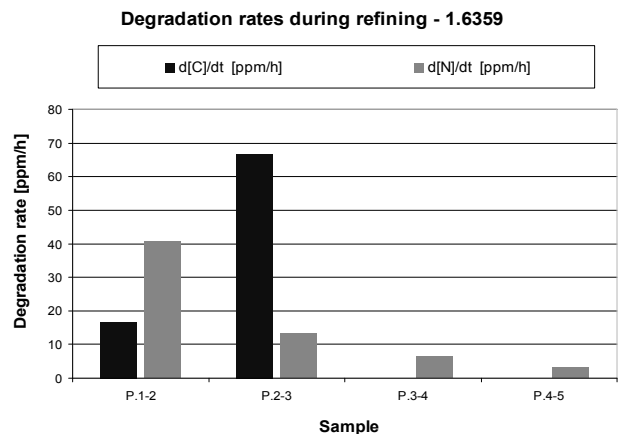Figure 4: Decarburisation rate and rate of nitrogen removal during refining of 1.3551

Figure 5: Decarburisation rate and rate of nitrogen removal during refining of 1.6359

CO-equilibrium

According to the chemical reaction shown above, carbon and oxygen form carbon monoxide {CO} as soon as the charge starts melting under vacuum pressure. Figures 6 and 7 show the chemical analyses (calculated and measured) during the refining period and the theoretical equilibria calculated for different pressures and steel grades. The reaction starts for booth steel grades at the calculated composition "Ch.". Carbon and oxygen content decreases due to CO-boiling to reach the final process equilibrium P.4 along the blue, dashed line. This dashed line is entitled "C/O = 12/16" and indicates the ratio of molar mass of carbon over oxygen (12/16).

Decarburisation/deoxidation must proceed along this line according to the stoichiometric CO-formation reaction.

As shown in Figures 6 and 7, booth steel grades, regardless of low or high carbon content, do not reach thermodynamically equilibrium. At refining end (sample P.4), when no CO bubbles can be determined any more and the carbon content keeps constant, the corresponding equilibrium pressures are in the range of 0.01bar although the VIDP melting chamber pressure is lower than 0.0001bar. The final sample of Maraging steels lies closer to the theoretical equilibrium compared to the high carbon bearing steel.
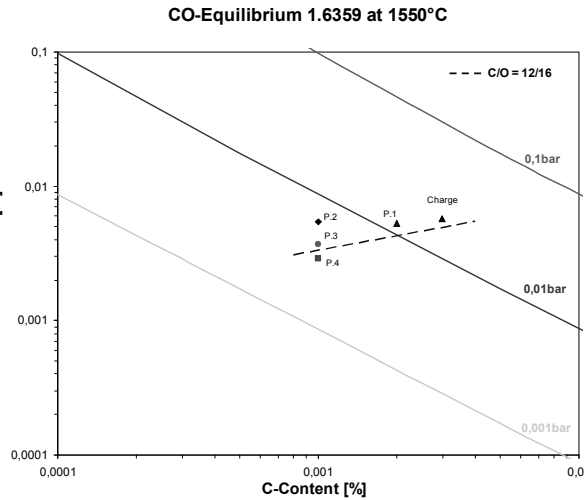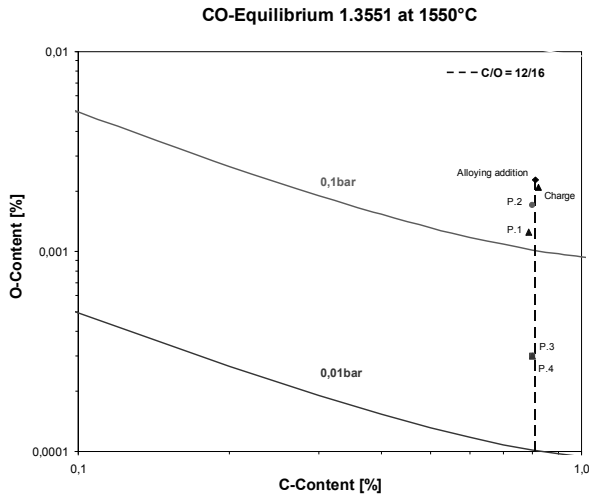

Figure 6: CO-equilibrium (1.3551 ....

Figure 7: CO-equilibrium (1.6359)
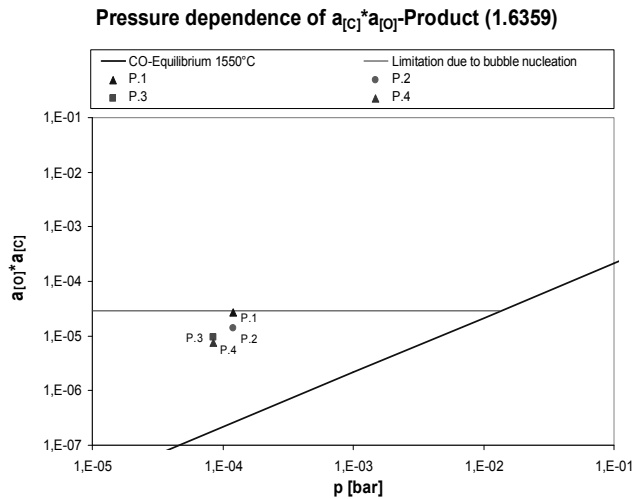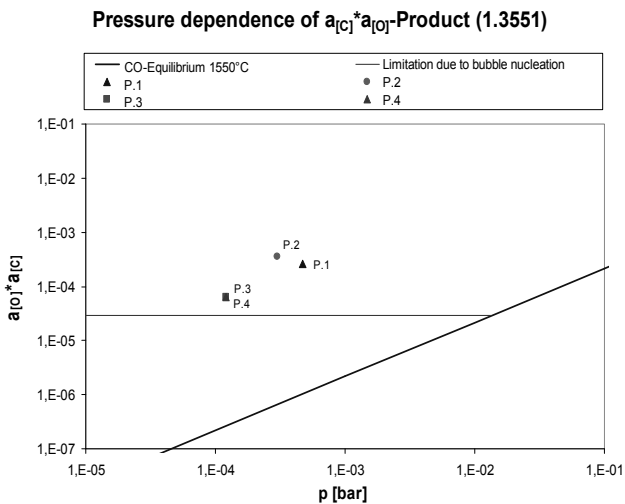

Figure 9:Pressure dependence of a[C]*a[O]-product(1.3551)

Figure 10: Pressure dependence of a[C]*a[O]-product (1.6359)

Figure 8 illustrates a summary over all investigated steel grades at the end of the refining period. Calculated and theoretical CO-equilibrium lines at different pressures from 0.0001bar to 1bar are compared with carbon and oxygen measurements of five different steel grades at refining end. As explained before, calculated equilibriums are not reached during vacuum treatment in

the VIDP-process. Maraging steels are closer to the theoretical values than the corrosion resistant martensitic steel and the bearing steels. The grey line, connecting the five alloys indicates the VIDP-process equilibrium – a quasi-stationary condition – what means, that lower carbon and oxygen contents are not reachable by the VIDP-process and its current set-up.
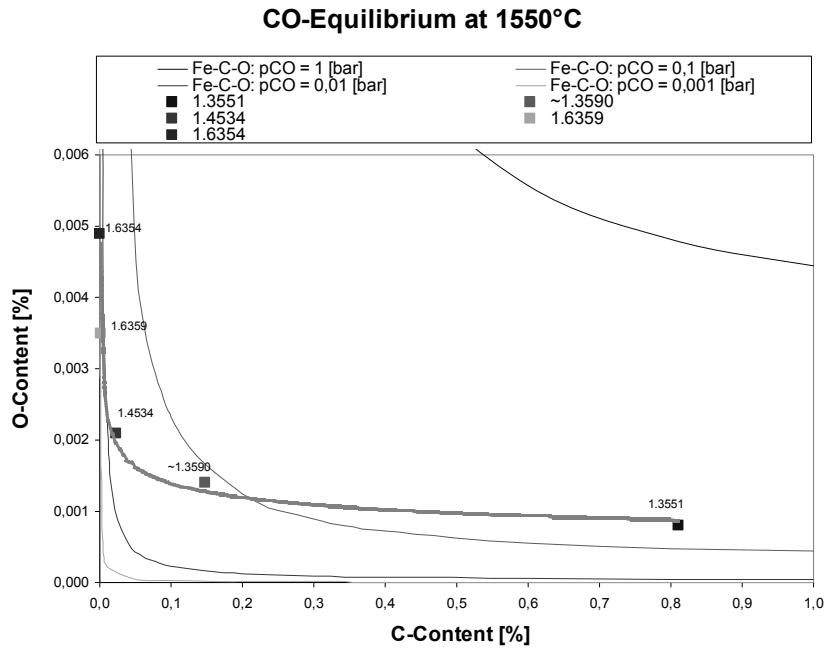
CO-Equilibrium at 1550°C

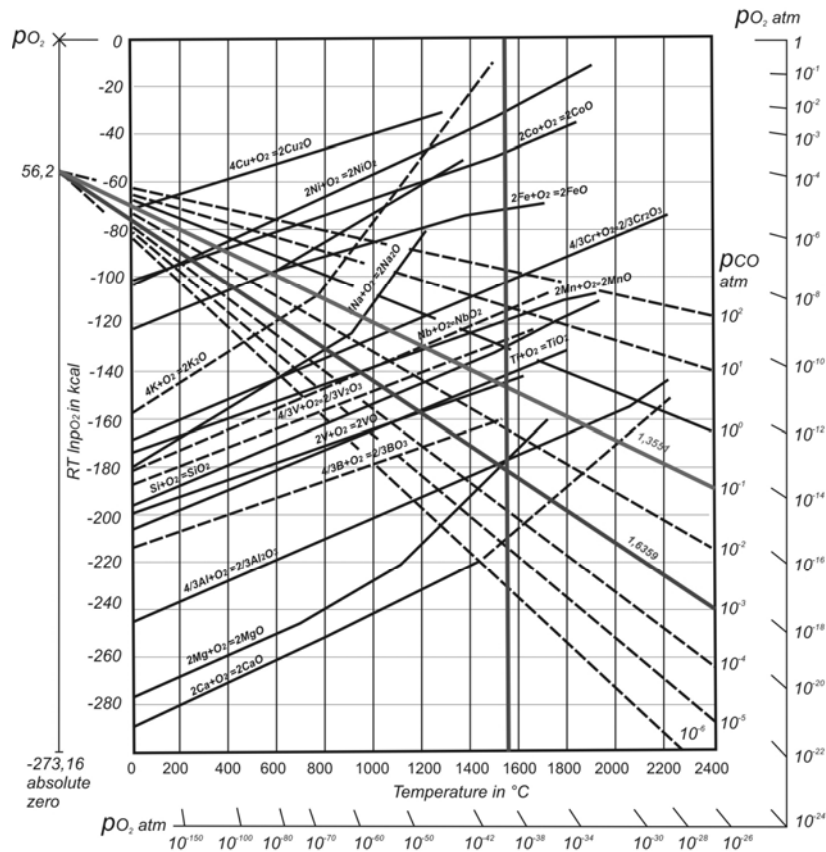*Figure 8: CO-process equilibrium (several alloys)*

Figure 11: Free energy diagramm for oxides [7]

Limitations

Decarburisation/deoxidation due to CO-formation is a pressure dependent reaction as explained in Figure 1 – the lower the pressure the lower the product of carbon and oxygen activity $a_{[C]}*a_{[O]}$ according to the thermodynamic theory. But in reality the decarburisation/deoxidation in vacuum plants stops at carbon and oxygen contents corresponding to pressures in the range of 0.001 to 0.1bar although the vacuum pressure is much less. Reasons therefore are amongst others

- Nucleation and bubble formation

- Oxygen supply by reduction of refractory material

Nucleation and Bubble Formation

It's well known that nucleation and bubble formation requires a minimum pressure inside a bubble nuclei p_{min} which has to be higher than the atmospheric pressure p_A, the ferrostatic pressure p_{Fe}, and the capillary pressure p_σ.

$$p_{min} = p_A + p_{Fe} + p_\sigma$$

The atmospheric pressure can be reduced due to vacuum treatment. The ferrostatic pressure is less directly under the melt surface. Since the capillary pressure increases if the radius of the bubble nuclei decreases a critical radius rk is necessary for bubble growing which can be found in a bath depth h=2rk. The minimum bubble pressure pmin therefore is given as a function of density and surface tension. For iron based alloys pmin can be calculated to 0.0133bar. Furthermore the product of carbon and oxygen activity a[C]*a[O] can be calculated to 3*10-5 [6].

Our investigations are in a good agreement with theory as Figures 9 and 10 point out. Especially the final sample P.4 of the bearing steel is close to the red line indicating the limitation due to bubble nucleation. The a[C]*a[O] – product as well as the equilibrium pressure is lower for the maraging steel (1.6359) than for the bearing steel (1.3551) as expected from Figure 8.

Oxygen Supply by Reduction of Refractory Material

A comparison of equilibrium CO-pressures at the end of refining with the equilibrium CO-pressures corresponding to the free energy of oxides (shown in Figure 11) indicates, that low carbon alloys with low CO-partial pressures are able to reduce alumina and magnesia at melting temperatures in the range of 1550°C. Figure 11 explains that the refractory lining material is reduced while melting maraging steels and an oxygen transfer to the melt is given. That's why no lower carbon and oxygen contents are possible during melting of maraging steels.

Summary and Conclusions

The production of special steels and superalloys requires VIDP melting and treating due to high cleanliness. To guarantee lowest carbon or oxygen contents vacuum-deoxidation/decarburisation during the refining period is of high importance. Vacuumdeoxidation/decarburisation is pressure dependent and can reach high deoxidation/decarburisation levels. Due to the gaseous reaction product carbon monoxide {CO} non-metallic inclusions do not occur. However, the CO-formation reaction stops between pressures of 0.001 to 0.1bar although the vacuum pressure is less. Vacuum-deoxidation/decarburisation is limited by nucleation and bubble formation (a[C]*a[O]-product) and oxygen supply by reduction of refractory material.

The investigations were carried out by examination of five different alloys to cover a wide range of carbon contents between 0,001 and 0.8%. The charging materials analyses were calculated and four samples were taken during refining period.

Carbon and oxygen contents decrease during refining due to the vacuum treatment and CO-formation. The rate of carbon and oxygen degradation is high at the very beginning of the process but the analyses keep constant when the process equilibrium is reached. The removal of nitrogen is high if the CO-reaction is in progress but decreases to very low rates without CO-bubbling.

CO-equilibrium diagrams show that high carbon alloys reach lowest oxygen levels and process equilibria around 0.01 and 0.1bar. On the other hand low carbon alloys have higher oxygen contents and the equilibria CO-pressures are between 0.001 and 0.01bar.

The a[C]*a[O]-product is an indicator for progress of vacuum-deoxidation/decarburisation which is limited by nucleation and bubble formation. Low carbon alloys reach lower a[C]*a[O]-products than high carbon steels

The equilibria CO-pressures of low carbon alloys are in the range of 0.001bar. Those low CO-pressures are able to reduce alumina and magnesia and limit vacuum-deoxidation/decarburisation by oxygen supply.

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