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Simulation of the carbides precipitation mechanism in 34CrMo4 and 42CrMo4 steels

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Abstract: The low-alloyed Cr-Mo steels (25CrMo4, 34CrMo4 and 42CrMo4) are used for production of important technical equipment parts in the petrochemical industry, for transportation of the gaseous hydrocarbons, concentrated acids, and lyes. They are also used for rolling of seamless tubes, in the production of pressure bottles, steel bolts, etc. Steel grades 25CrMo4 and 34CrMo4 represents materials with improved mechanical properties, mainly due to vanadium microalloying. Unfortunately, vanadium microalloyed steels are very sensitive to cracks occurrence after continuous casting and/or heating before hot rolling. This paper deals with vanadium rich precipitates MC, M_3C_2 and M_7C_3 formation during continuous casting process. It was verified that vanadium microalloyed steel 34CrMo4 exhibited different carbides formation mechanism and contained significantly higher rate of vanadium in M_xC_y carbides than steel grade 42CrMo4 using experimental data and ThermoCalc software. Understanding of the vanadium precipitation kinetics is necessary for manufacturing process optimization and internal defects limitation.

Keywords: Cracks, Precipitation, Vanadium, 34CrMo4, 42CrMo4

1. Introduction

Vanadium microalloyed steel grades 25CrMo4 and 34CrMo4 are commonly produced under the same conditions as 42CrMo4 steel. The only relevant difference among these steel grades is vanadium content. Based on the manufacturing experience it was discovered that 24CrMo4 and 34CrMo4 steels are significantly more sensitive to the cracks that occurred after continuous casting and/or heating in the soaking pit [1-5]. Critical points of the manufacturing process were already identified. Among them there is the enormous overheating temperature in the tundish [6], the low steel casting speed, the occurrence of central segregations [7], the non-uniform intensity of secondary cooling during casting, the insufficient reduction of central parts of the rolled stock [1], the unsuitable interval of the forming temperatures [8], and the non-uniform friction between the rolled stock and the roll [8]. Statistical analysis, artificial neural networks, finite elements methods, microchemical analysis and mictrostructure study led to successful reduction of the internal cracks occurrence [9-11].

Precipitation of the vanadium is carried out by creation of VN, V(C,N) and precipitation of VC occurs only after exhaustion of nitrogen stocks in steel. In reality, pure vanadium nitrides can be observed rarely. The most frequently, carbonitrides complexes can be observed, C/N rate is determined by the availability of nitrogen. In the initial stage of precipitation, when amount of the nitrogen is high enough the carbon content in V(C,N) represent about 5% of the carbonitride weight and with decreasing availability of nitrogen, this rate is growing [12]. When the temperature 1193 K is achieved there is no longer any nitrogen available. Below this temperature, vanadium precipitates only in the form of VxCy. Vanadium precipitation is completed at about 973 K [13].

In terms of the VC, VN and V(C,N) precipitation mechanism it is possible to state that the precipitation occurs in the stable austenite through heterogeneous nucleation of the VC, VN and V(C,N) on the dislocations, austenite grain boundaries and the MnS particles [2,3]. In many cases it can arise even complex multiphase inclusions, it is possible to observe multiphase inclusions such as MnS, (Ti,V) (C,N) and AlN [14]. The negative effect of precipitation of carbides, nitrides and carbonitrides of vanadium is realized during the continuous casting, if the proper casting conditions are not guaranteed. Continuously cast blooms straightening within the critical temperature range (1073 – 1273 K) on the radial casting machines creates unfavourable stress-strain conditions that contributes to the initiation and propagation of the internal cracks [1-3]. Typical internal defect present in 34CrMo4 steel after hot-rolling is shown on Fig.1.

Figure 1. *Transverse cut of the hot-rolled billet made from 34CrMo4 steel with internal defect.*

This paper deals with ThermoCalc calculations that allow qualitative and quantitative prediction of the newly created precipitates.

2. Materials and Methods

Two low-alloyed Cr-Mo steel grades, namely 34CrMo4 and 42CrMo4, were chosen for calculation of the precipitation kinetics parameters. Typical chemical composition of the studied steels is shown in Tab.1.

Table 1. *Chemical composition of low-alloyed Cr-Mo steels (wt. %).*

Steel	C	Mn	Si	P	S	N	Cr	Ni	Mo	V
34CrMo4	0,34	0,74	0,25	0,015	0,005	0,008	1,17	0,25	0,20	0,088
42CrMo4	0,42	0,74	0,25	0,015	0,005	0,008	1,18	0,25	0,20	0,005

ThermoCalc 3.1 software and it´s material databases were used for calculations of the vanadium mass percentage content in M_xC_y precipitates. The studied variables were precipitation profile with respect to the low ductility zone and vanadium content M_xC_y precipitates. The samples taken from both steel grades (transverse cut of the continuously cast bloom) were cooled down in liquid nitrogen (77 K) and broken by Charpy impact tester. Fracture surface of analyzed steels were studied using SEM TESCAN Mira. Extraction carbon replicas were prepared by etching (10% HNO_3 in alcohol, 298 K, voltage 10 V). Thereafter, the replicas were studied by TEM JEM 200CX and minority phases were identified by EDX X-rays microanalysis.

3. Results and Discussion

Due to the absence of the titanium in above discussed steel grades it can be expected that most of the vanadium atoms precipitates in form of the VN in case of both 34CrMo4 and 42CrMo4 steels. This process occurs during continuous casting predominantly at higher temperatures, than are typical for low ductility zone.

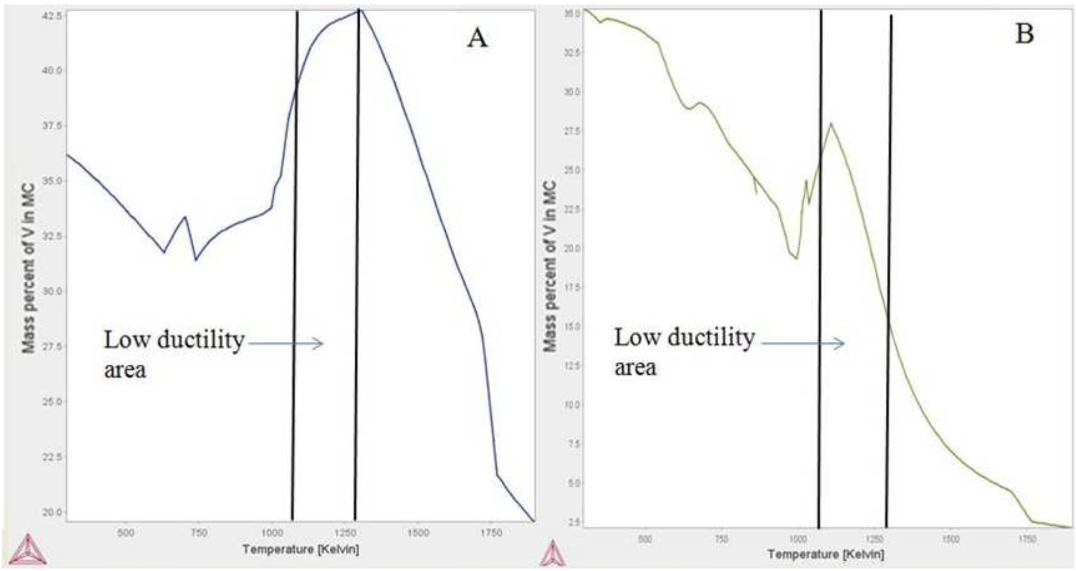

Figure 2. *Mass percent of the vanadium that precipitated in form of the VC, A – 34CrMo4, B – 42CrMo4.*

Because of this fact negative effects of the vanadium precipitation during the continuously cast blooms straightening is very significantly reduced. In case of the 34CrMo4 steel vanadium/nitrogen rate is high enough for precipitation of the carbides and carbonitrides. Most of the “free” vanadium which is available in the austenite when the nitrogen resources are exhausted, precipitates in form of the VC and/or relevant multiphase carbides and carbonitrides, see Fig.2A,B.

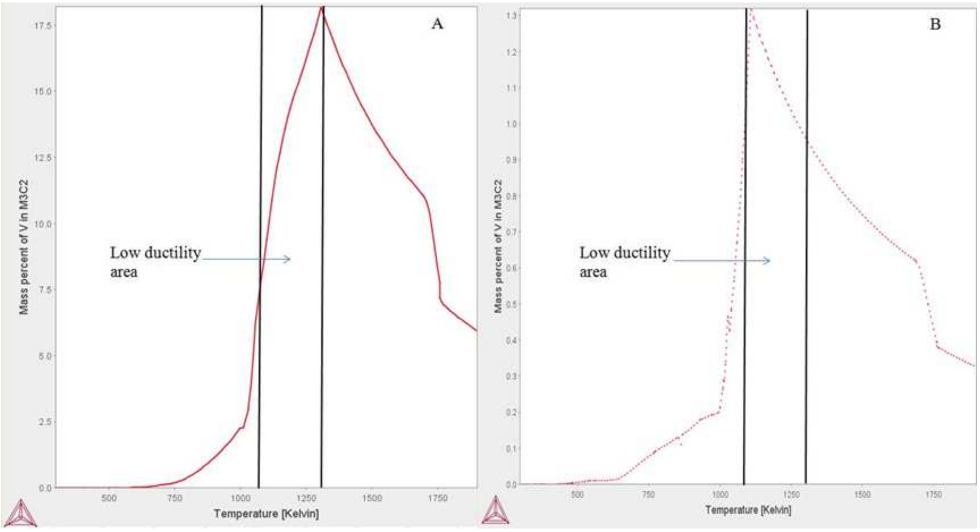

Figure 3. *Mass percent of the vanadium that precipitated in form of the* V_3C_2*, A – 34CrMo4, B – 42CrMo4.*

Meanwhile, vanadium content in VC precipitates is quite high even in 42CrMo4 steel, in case of the V_3C_2 and relevant multiphase carbides and carbonitrides, 34CrMo4 steel contents almost 14 times higher amount of vanadium in form of V_3C_2 precipitates compared to the 42CrMo4 steel, see Fig.3.

Formation of the V_7C_3 carbides exhibited similar trend that was observed in case of V_3C_2. 34CrMo4 steel contains still sufficient amount of vanadium for precipitation of V_7C_3 carbides, however, vanadium content in 42CrMo4 steel is almost exhausted. Although, even in 34CrMo4 steel vanadium content decreases with decreasing thermodynamical stability of the precipitates, see Fig. 4.

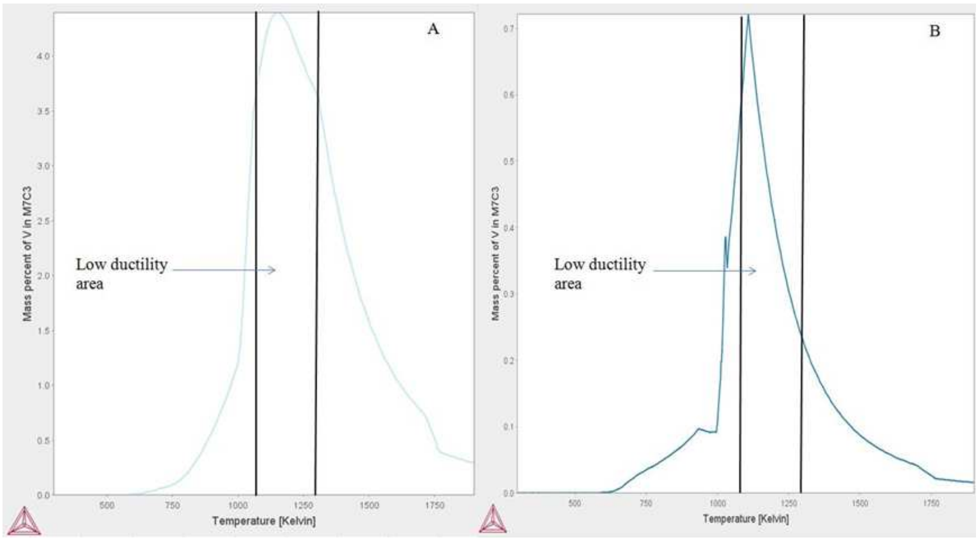

Figure 4. *Mass percent of the vanadium that precipitated in form of the* V_7C_3*, A – 34CrMo4, B – 42CrMo4.*

Due to the fact that 34CrMo4 steel is very sensitive to the internal defects occurrence, prediction possibilities of the ThermoCalc software were compared with the results of TEM analysis of the extraction replicas. ThermoCalc claimed that chrome will be present in form of $M_{23}C_6$.

This result was fully confirmed by extraction replicas analysis. Chrome was present especially in form of $Cr_{23}C_6$ precipitates both for specimen taken form bloom´s surface and internal part, see Fig. 5.

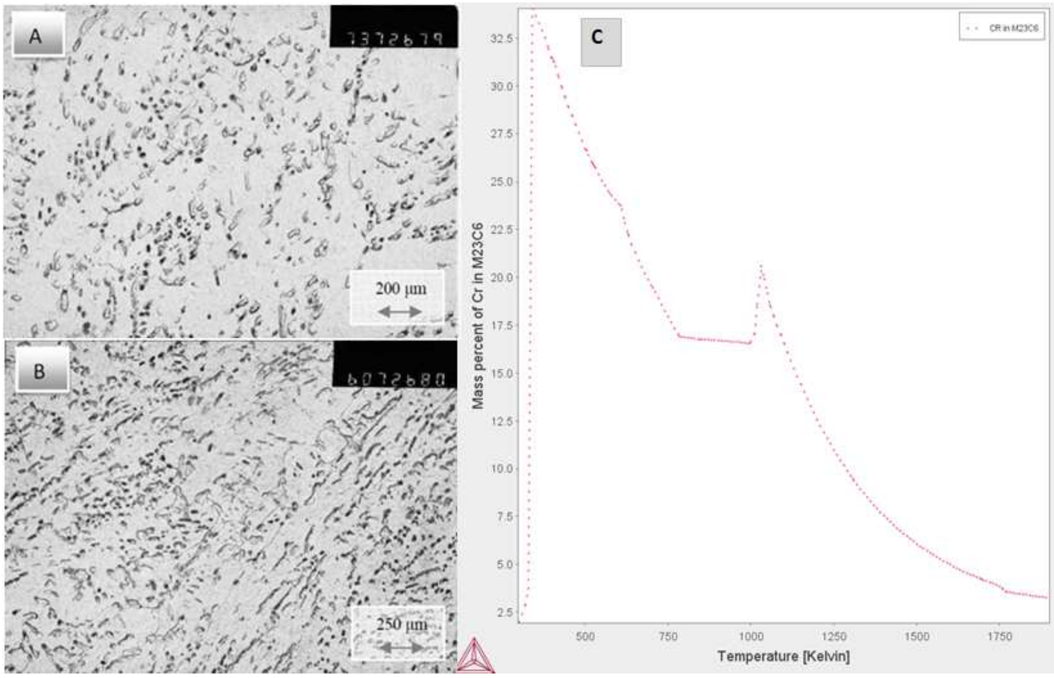

Figure 5. *TEM images of the 34CrMo4 steel represent precipitates distribution in the internal crack surrounding. A – bloom surface, B – bloom center, mass percent of the chrome that precipitated in form of the* $Cr_{23}C_6$.

Although, ThermoCalc represents useful tool for qualitative and quantitative phase analysis, it does not allow to take into account influence of steel heterogeneity. For more accurate results it is beneficial to realize at least two microchemical analysis for internal and surface parts of the studied material.

4. Conclusions

Calculation of the precipitation kinetics represents perspective trend in expansion of the methods that can be used in material research. ThermoCalc simulations were used for prediction of the precipitation characteristics of the 34CrMo4 and 42CrMo4 steels. In this paper it was demonstrated that even small difference in steels chemical composition can be responsible for the serious manufacturing problems such as internal cracks occurrence in low-alloyed Cr-Mo steels. ThermoCalc calculations were mainly focused on vanadium carbides that are responsible for internal cracks initiation and propagation if favourable production conditions cannot be guaranteed. ThermoCalc calculations can be used not only for description and explanation of precipitation process but also allow to simulate possible steel´s chemical composition modifications without necessity of the material production and structural analysis.

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