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Ti微合金化高强耐候钢的 冶炼工艺及强化机理研究

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Metallurgical Process and Strengthening Mechanism of Ti Microalloyed High-Strength Weather-Resisting Steel

Candidate: Li Liejun

Speciality: Ferro-Metallurgy

Supervisor: Zhai Qijie

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上海大学

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族

答辩委员会对论文的评语

李烈军同学在查阅了大量国内外相关文献基础上,根据企业发展和市场需求选择"Ti 微合金化高强耐候钢的冶炼工艺及强化机理研究"作为博士论文研究课题,选题符合薄板坯连铸连轧技术及微合金化技术研究的发展动向,具有重要的理论意义和应用价值。

论文从成分设计开始,通过大量的现场试验和理论分析,研究了 Ti 微合金化高强耐候钢的冶炼工艺、铸坯质量、组织和性能、析出物及强化机理,取得了以下创新性成果:

- 1. 系统研究了影响 Ti 回收率的因素,通过严格的冶炼工艺控制,使钢中氧、氮、硫在较低的水平,并采用全保护浇注,有效地提高了 Ti 的回收率,加 Ti 铁的 Ti 回收率稳定在65wt%以上,同时避免了连铸过程中的水口结瘤。
- 2. 阐明了薄板坯连铸连轧各工艺阶段 Ti 化合物的析出规律,对碳化钛和氮化钛的结构、尺寸、形貌和粒度分布有了全面的认识。
- 3. 研究表明, Ti 微合金化高强耐候钢中合理的 Ti 含量范围为 $0.04\%\sim0.12\%$, 并在薄板坯连铸连轧生产线上开发出了屈服强度超过 600 MPa 的 Ti 微合金化高强耐候钢。
- 4. 研究表明, Ti 微合金化高强耐候钢比普通集装箱板强度大幅度提高的主要原因是 TiC 的沉淀强化作用。

该论文思路清晰,工作量大,数据可靠,理论分析及应用分析深入、系统,条理清楚,文笔流畅,表明作者已经掌握了本学科坚实宽广的基础理论和系统深入的专业知识,具有很强的独立从事科学研究和应用研究的能力。答辩过程中, 叙述清晰,回答问题正确。

答辩委员会表决结果

答辩委员会通过无记名投票,一致同意通过李烈军同学的博士学位论文答辩,并建议授予工学博士学位。

规律,对碳化铁和氧化铁粉均加、尺寸、形貌和粒度分布有了

4.5. 研究表明, Ti 從合全化高强耐候制中全理的 Ti 会

答辩委员会主席

2005年8月26日

以 Cu-P-Cr-Ni 普通集装箱板为基础,通过严格的工艺控制,在薄板坯连铸连轧生产线上首次成功开发了 Ti 微合金化高强度耐候钢,屈服强度超过 600 MPa。采用电子显微分析技术、化学相分析等多种实验手段研究了高强耐候钢的组织,尤其是碳氮化物析出,阐明了该钢种的强化机理。得到主要结论如下:

Ti 微合金化高强耐候钢的成分设计根据电炉—CSP 的特点,利用废钢中的 Cu、P、Cr、Ni 等残余元素,在钢中添加较便宜的 Ti 铁,具有明显的成本优势。采用了低氧、低氮、低硫的控制技术,生产出高洁净钢。通过对电炉、出钢过程和精炼过程的严格工艺控制降低钢中的氧含量,并在精炼过程中用 Al 深脱氧后再加入 Ti,提高了 Ti 铁回收率,使其稳定在 65%以上。

薄板坯的低倍组织由表面激冷层和中心区域发达的树枝晶组成,连轧前奥氏体晶粒大多在 500~1 000 μm 范围内;薄板坯表面质量较好,心部存在中心疏松、微小裂纹等缺陷;微合金添加元素 Ti 在铸坯中的分布极为均匀,铸坯宽度方向两端 C元素偏析较明显。

带钢的强度随钢中 Ti 含量增加、带钢规格减薄而显著增加。 开轧温度在 1050~1120℃范围内变化对组织和性能没有影响, 终轧温度和卷取温度的合理范围约为900℃和600℃。Ti 微合金 化高强耐候钢的通卷性能良好。Ti 微合金化高强耐候钢中合理 的 Ti 含量范围为 0.04%~0.12%, 屈服强度为450~600 MPa。

高强耐候钢中存在 TiN、TiC 和 $Ti_4C_2S_2$ 等大量析出物。 TiN 形貌为方形或不规则形状,尺寸从几十纳米到数微米;TiC 呈球形,尺寸从几纳米到几十纳米不等,在铁素体基体中和位错线上大量弥散分布。热力学计算表明,连轧前 TiN 的析出过程已基本完成,而 TiC 在奥氏体的低温区或铁素体中析出。薄板坯凝固和冷却速度快的特点使 TiN 析出物更加细小,而 TiC 的析出机制还需要深入的研究。

由于 Ti 固定了钢中的自由氮,形成细小的 TiN 颗粒,改善了高强耐候钢的冷弯性能和焊接性能。焊接后试样拉伸时均在母材部位断裂,在焊缝处为块状先共析铁素体和大量的魏氏体组织,以及分布于铁素体之间的珠光体。高强耐候钢的耐候性能良好。

高强耐候钢具有良好的冲击韧性,韧脆转变温度较低,但 TiC 析出物在一定程度上损害了钢材的韧性。随着钢中 Ti 含量增加,同样温度下带钢的冲击韧性降低;随 Ti 含量增加,带钢的韧脆转变温度升高。

化学相分析表明,随着钢中 Ti 含量增加,MC 相的质量分数增加,M₃C 相的质量分数减少,而 MC 相中碳元素的含量明显增加。采用 X 射线小角散射测定了 MC 相的粒度分布,0.068wt% Ti 钢中 $1\sim10$ nm 范围内析出相的质量分数占总析出相(统计范围为 $1\sim300$ nm)的 63.4wt%,这些析出物粒子主要是TiC,根据 Orowan 机制计算了沉淀强化增量,约为115 MPa。

Ti 微合金化高强耐候钢有晶粒细化、沉淀强化、位错强化和固溶强化等多种强化方式,除沉淀强化机制外,其他强化机

制叠加后的屈服强度约为 430 MPa。除元素 Ti 外,高强耐候钢和普通集装箱板的化学成分基本相同,而屈服强度却大为提高,主要原因为 TiC 的沉淀强化作用。

关键词 薄板坯连铸连轧;微合金化技术;碳氮化物;沉淀强化

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the mich structure of steels especially the precipitation. The

developed by utilizing the residual elements including Cu. P.

Abstract

High-strength weather-resisting steel, based on the container strip with the composition of Cu-P-Cr-Ni and titanium additive, had been successfully produced by thin slab casting and rolling (TSCR), through strictly controlled smelting and rolling process for the first time. The experimental methods, such as metalloscopy, electron microscopy and chemical phase analysis, were used to study the microstructure of steel, especially the precipitation. The strengthening mechanism of microalloying steel caused by TSCR was clarified. The main conclusions could be summarized as follows:

Aiming at the characteristic of EAF-CSP process, low cost yet high-strength weather-resisting steel had been developed by utilizing the residual elements including Cu, P, Cr, and Ni etc. contained in the used scrap steel in combination with the ferrotitanum addition. Steels with high purity were produced through strictly controlling for the content of oxygen, sulfur and nitrogen. Moreover, the recovery ratio of ferrotitanium can be stabilized above 65% attibuted to the titanium addition into the steel after deep deoxidization by aluminium.

The macrostructure of the thin slabs were consisted of

the surface chill layer and central developed dendrites. Before rolling, the size of the austenitic grains was in the range of $500\sim1~000~\mu m$. As a result, the surface with better quality could be obtained, in spite of the shrinkage porosities and microcracks existed in the central zone. The additive Ti was uniformly distributed in the thin slab, however, obvious segregation of C elment could be observed in the width direction of the thin slab.

The strength of the strip was remarkably increased with increasing Ti content in steel yet decreasing strip thickness. No perceptible change of the microstructure and properties of strips could be observed when the rough rolling temperature fluctuated from 1.050° C to 1.120° C. In particular, the finish rolling temperature and coiling temperature were controlled to be about 900° C and 600° C respectively, by which uniform mechanical properties could be gained in the whole strip coil of the high-strength weather-resisting steel. The reasonable content of titanium in steel was about 0.04wt% ~ 0.12 wt% and correspondingly the yield strength could be attained $450\sim600$ MPa.

Large amount of precipitation, such as TiN, TiC and $Ti_4C_2S_2$ has been found in the high-strength weather-resisting steels produced by TSCR. The TiN particles, in square or irregular shape, had the sizes in the range of tens of nanometers to several microns. In contrast, the sizes of the spherical TiC particles remained in the range of several to tens of nanometers, distributed along the grain boundaries

and in the ferrite matrix. The thermodynamic calculation showed that the precipitation of TiN should be finished before continuous rolling, yet the TiC was precipitated in the low temperature zone of austenite and the ferrite. The TiN particles could be refined due to the inherent characteristics e. g. high cooling rate of the solidification of thin slabs. However, deep investigation was still necessarily to be conducted for the mechanism TiC precipitation.

Due to the fixation of free nitrogen by Ti, refined TiN particles could be formed, and therefore the cold bendability and weldability of the high-strength weather-resisting steel can be improved. After welding, the testing specimen was always fractured at the site of base metal. The structure of the welded seam was consisted of the blocklike pro-eutectoid ferrite and a mass of Widmanstaten structure as well as the perlite distributed among the ferrite. In sum, the developed high-strength weather-resisting steel possessed good weather-resisting property.

Besides, the high-strength weather-resisting steel possessed good impact ductility and lower ductility-tough transition temperature, but the TiC precipitates could damage its ductility. Given the temperature, the impact ductility was decreased with increasing the Ti addition. Correspondingly, the ductility-tough transition temperature was enhanced with increasing the Ti addition.

The results of chemical phase analysis showed that the mass fraction of MC phase increased and that of M₃C

decreased, yet the carbon content in MC phase was increased and the nitrogen content was decreased with increasing titanium in the steel. Employing small angle X-ray scattering, the size distribution of MC phase was measured. The results showed that the particles smaller than 10 nm are mainly TiC ones, occupied 63.4wt% of the totally precipitated phases (Stastical range: $1\sim300\,\mathrm{nm}$). The calculation result according to Orowan mechanism indicated that strength contribution of precipitation hardening was about 115 MPa for the 4 mm-thick strip with 0.068%Ti.

The main strengthening manners in high-strength weather-resisting steels included grain refinement, precipitation hardening, dislocation hardening and solution strengthing etc. Compared with those conventional container strips, similar composition were adopted except Ti element, which could cause precipitation hardening. Except precipitation hardening, the ultimate combined strength was only about 430 MPa on condition that the other strengthening manners were taken into account. Thus, it is reasonable to come to the conclusion that the main reason for high strength of Ti microalloyed high-strength weather-resisting steel was precipitation hardening that resulted from TiC particles.

Key words thin slab casting and rolling; microalloying technology; carbonitride; precipitation hardening

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