

DIRECT ALLOYING OF STEEL: A REVIEW OF PLANT EXPERIENCES AND LAB STUDIES*

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Abstract

The direct alloying of the steel is attractive as it minimizes alloying cost, total energy consumption and CO₂ emissions, compared with ferroalloys. This alloying technique is in use for high alloyed (stainless), low alloyed and carbon steel. The elements reviewed include chromium, nickel, molybdenum, vanadium and manganese. Raw materials used to this purpose are lump ores, ore fines, special slags, self-reducing briquettes and others. For the development of this technique, tools like thermodynamic modelling, testing in induction furnaces of several scales and industrial tests have been instrumental. This paper summarizes the fundamental and industrial efforts carried out to develop and employ direct alloying in Japan, Russia, China and other steelmaking countries.

Keywords: Direct alloying; Chromium; Manganese; Vanadium.

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1 INTRODUCTION

Direct alloying has been around for at least three decades. It attracted some steel companies because of the expectations in lower cost, total energy consumption and total CO₂ emissions, in comparison with the use of ferroalloys. The drivers behind preparation of the review are

- A consult by a steel company testing in small scale manganese ore addition to replace ferromanganese, for production of rebar, wire rod and shapes (cDRI - EAF – LMF - billet casting)
- A consult by a steel company in order to lower ferroalloys cost for rebar steel production (EAF – LMF – billet casting)
- A request for information from a supplier to a stainless steel producer for use of chromite ore to replace FeCr (EAF – AOD – ingot casting)

For the preparation of the paper, a thorough review of direct alloying literature was carried out, including 42 full papers (see table 1). There were some other references which could not be obtained as full papers, most of them in Russian and Chinese.

Table 1. Summary of papers on direct alloying: country, plant and/or R&D center, element for direct alloying, year of publication and reference

Country	Plant	R&D Center	Elem.	Year	Ref.
China	-	USTB	Cr	2018	1
Japan	JFE Steel Chiba	-	Cr	2017	4
Russia		Siberian State University	V, Ba, Sr, Ni	2017	39
Sweden		Swerea MEFOS, Lulea Univ. Tech., KTH, USTB	Cr	2016	14
Japan	JFE Steel Chiba	-	Cr	2016	7
Sweden		Swerea MEFOS, Lulea Univ. Tech.	Cr	2016	15
Sweden		Lulea Univ. Tech.	Cr	2016	17
Russia		Yurga Inst. Tech, Siberian State Univ.	Ni	2016	31
Russia		Siberian State University	V, Ba, Sr	2016	36
Russia		Yurga Inst. Tech, Siberian State Univ.	Mn	2015	25
Egypt	-	CMRDI	Cr	2015	2
Russia		Siberian State University	V	2015	33
China	Shijiazhuang I&S Co.	Wuhan Univ. Science & Tech.	Mo	2014	29
China	Shijiazhuang I&S Co.	Wuhan Univ. Science & Tech.	V	2014	32
Sweden		Swerea MEFOS, Lulea Univ. Tech.	Cr	2014	18
Russia		Siberian State University	V	2014	38
China		USTB	W	2014	40
China	Shijiazhuang I&S Co.	Wuhan Univ. Science & Tech.	Mo	2013	26
Sweden		Jernkontoret, KTH	Mo	2013	28
Sweden		KTH, TU Bergakademie Freiberg	Cr	2012	16
Sweden	uddeholms AB	KTH	Mo	2011	30
Sweden		KTH	Mo	2010	27
Georgia	Georgian Manganese, Elektrovozostroitel	Tsereteli State University	Mn	2009	22
Russia		Far Eastern State University	Zr	2009	35
Japan	JFE Steel Chiba	-	Cr	2008	9
Japan	JFE Steel Chiba	-	Cr	2008	6

Cuba		University of Olguín	Mn	2007	19
Russia		I. P. Bardin Central Research Inst. Met.	Mn, Cr	2006	37
Russia	KMK Relsy, West Siberian Metallurgical Combine	Siberian State University	Mn	2004	23
Cuba		University of Olguin	Mn	2003	20
Mexico		National Polytechnic Institute	Mn	2003	21
China		Central Iron & Steel Res. Inst.	Mo,W, V	2000	41
Japan	JFE Steel Chiba	-	Cr	1997	3
Japan	JFE Steel Chiba	-	Cr	1997	5
UK	British Steel Teeside		Cr	1997	13
Japan	Kawasaki Steel Chiba		Cr	1994	12
Japan	Kawasaki Steel Chiba	-	Cr	1990	10
Japan	Kawasaki Steel Chiba	-	Cr	1990	11
URSS	Azovstal	Donetsk Polytechnical Inst.	Mn	1988	24
Japan	-	Toyohashi Univ. Tech.	Cr	1987	8
U.S.S.R.		UralNIChM	V	1971	34

The population of papers is segmented according to countries and elements in figures 1 and 2. Most papers on Direct Alloying come from USSR/Russia, Japan, Sweden and China. It should be pointed out that while most Japanese and Russian activity is related to industrial experiences, the Swedish activity is academic.

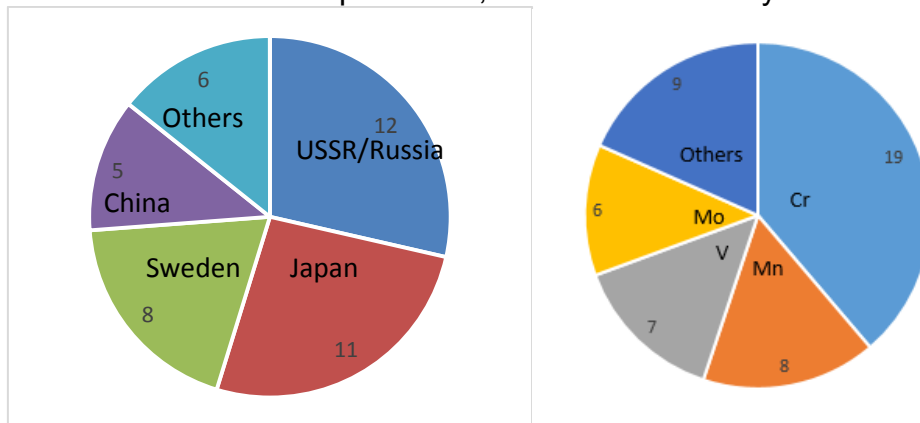


Figure 1. Left : Number of papers for each country, showing the dominance of Russia, Japan, Sweden and China. Right: Number of papers per element, showing the interest in Chromium, Manganese, Vanadium and Molybdenum

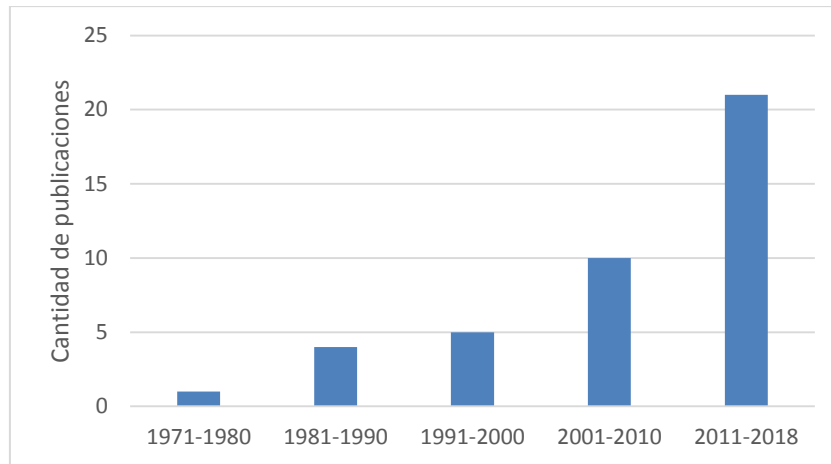


Figure 2. Number of papers published in different decades

In the following paragraphs, we discussed the four elements that had attracted more interest for direct alloying.

2 CHROMIUM

2.1 JFE Steel. This Japanese company (formerly Kawasaki Steel), has more than three decades of experience in direct alloying chromium for ferritic (and some austenitic) stainless steel. Production started in 1986 at Nishinomiya plant. The process included hot metal pretreatment, charging of hot metal, chromite pellets and coke in K-BOP I vessel, where smelting reduction proceeds. The alloyed hot metal was tapped into a hot metal ladle, slag was skimmed, and then the hot metal was charged to the K-BOP II vessel, where final decarburization took place. After tapping the steel onto the ladle, final refining was carried out in an RH unit, and then the ladle was sent to the slab caster (figure 3).

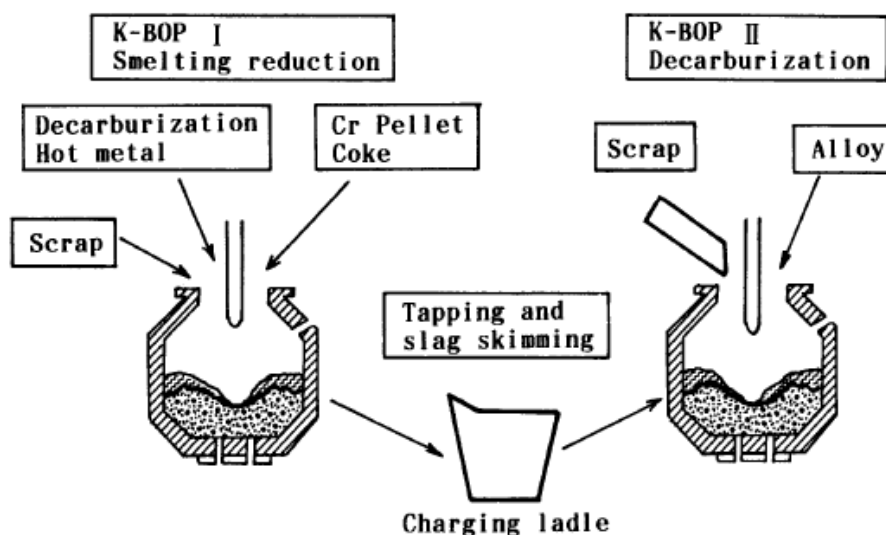


Figure 3. Lay out for direct alloying with chromite pellets for production of stainless steel in Kawasaki Steel Nishinomiya plant

By 1994, a new plant was started up in Kawasaki Steel Chiba (Chiba Nr 4). In this case, after hot metal pretreatment, the Smelting Reduction Furnace (SRF) was charged with the dephosphorized hot metal, and the injection of chromite sand (instead of dumping pellets as in Nishinomiya). Then the process proceeded further

in the decarburization furnace (DCF); ladle metallurgy was carried out at a VOD instead of the previous RH, and then slab casting.

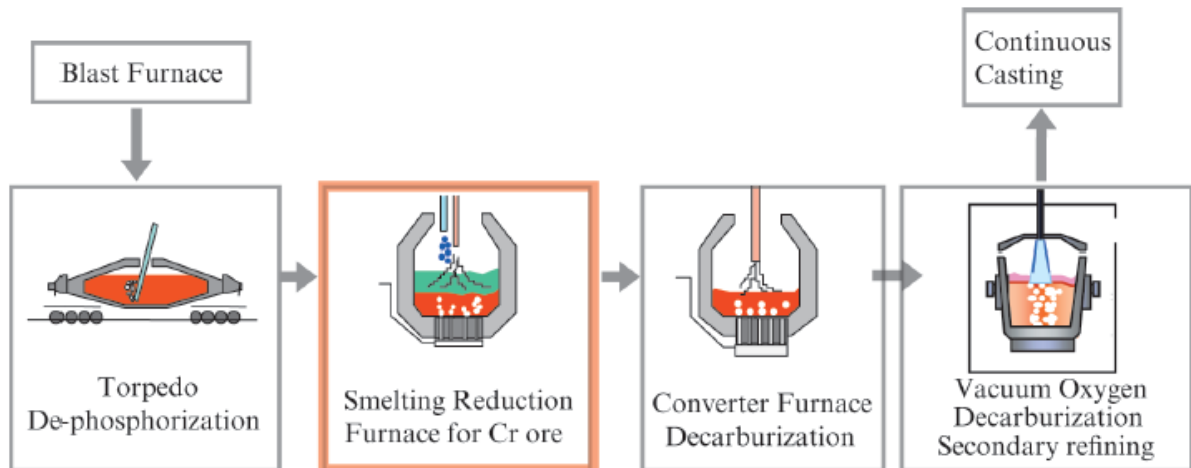


Figure 4. Lay out for direct alloying with chromite sand injection for production of stainless steel in Kawasaki Steel Chiba Nr. 4 plant

This plant was further optimized by installing a shaft furnace (called STAR furnace) using fine dust & slag to produce hot metal to be recycled to the smelting reduction furnace, recovering chromium units. A scrap and hot metal reservoir was installed, too (so-called J-FIRST), as a buffer metallic between the SRF and the DCF, see figure 5.

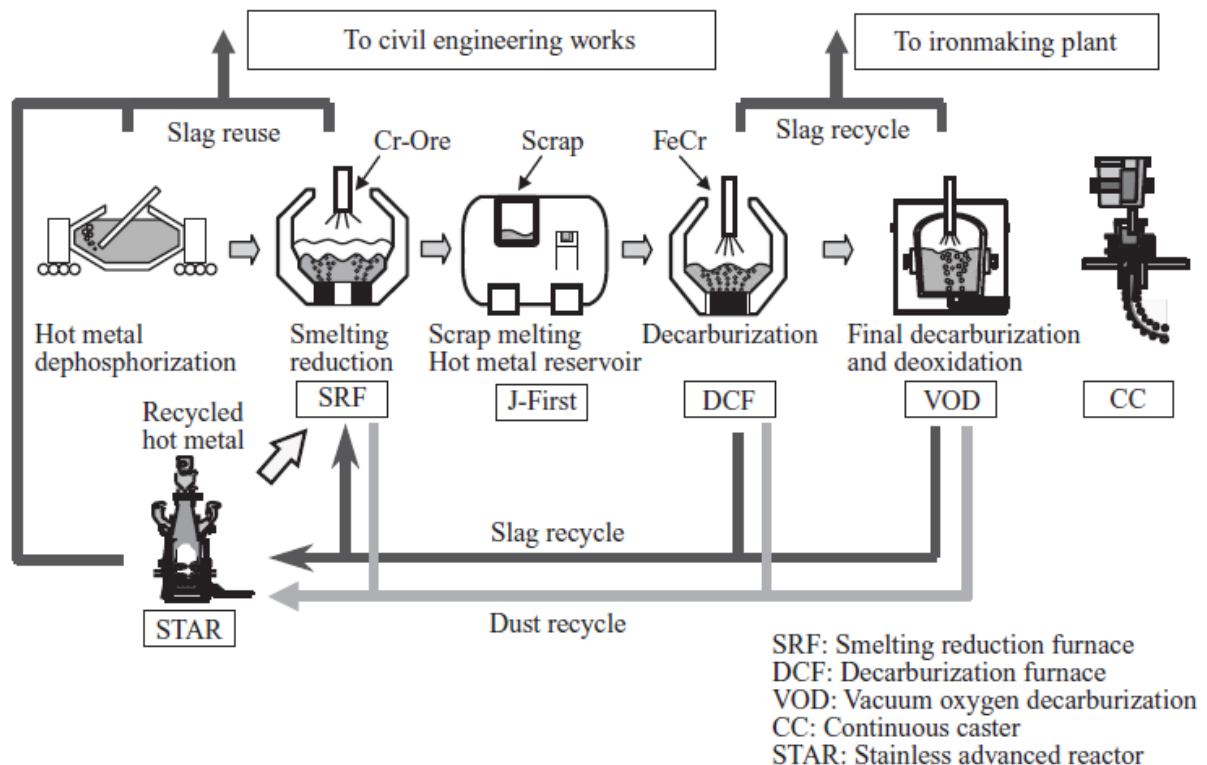


Figure 5. Introduction of slag and dust recovery in a shaft furnace (STAR), and of scrap melting and hot metal reservoir (J-FIRST)

Later on, efforts to decrease energy consumption were reported. First, higher oxygen supply as tested; but it brought about increased dust generation and lower Fe and Cr yield. Second, post combustion was tested, too. It also failed due to low heat transfer

and lower refractory life. Finally, a burner was designed for preheating the chromite sand while being injected to the furnace (figure 6, left). This was successful, lowering energy consumption 17% and in particular carbon consumption (figure 6, right).

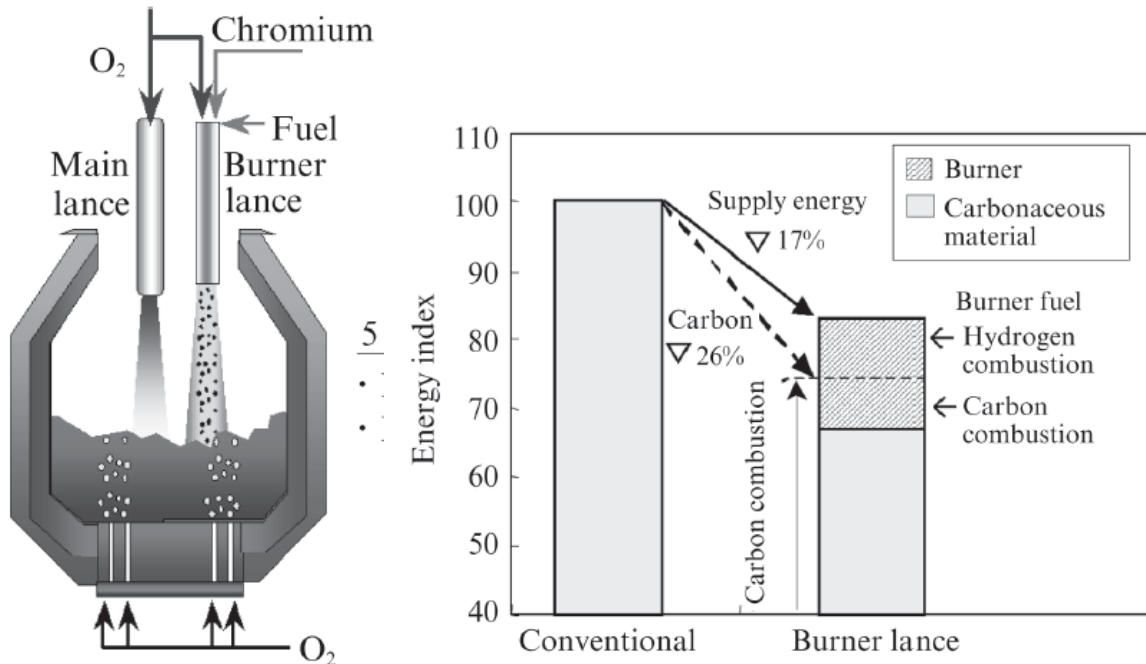


Figure 6. Left: Smelting Reduction Vessel with burner lance for the preheating of the chromite sand. Right: Decrease of energy consumption and carbon usage due to the introduction of the burner lance

This seems to be by far the most successful experience of direct alloying. There is some set of specific conditions driving to this situation:

- ✦ Lower energy requirements for oxygen steelmaking, due to low use of scrap
- ✦ Typical Japanese hot metal pretreatment: desiliconization and dephosphorization
- ✦ Availability of chromite sand for injection
- ✦ Introduction of dust and slag recovery in a dedicated furnace, to recover Cr loss to dust and slag
- ✦ Further improvement in energy consumption with the introduction of the lance burner to keep the process competitive

It is interesting to point out that simultaneously with this development, and in parallel with the second oil crisis, Kawasaki Steel replaced a group of Submerged Arc Furnaces for a Mini Blast Furnace, for the production of ferromanganese [43].

2.2 British Steel Teeside R&D. In the late nineties, probably after knowing about the Japanese success, there was a research program in this company to develop a process for smelting reduction of chromite ore using coal and oxygen. After a theoretical assessment, an experimental program was carried out in two different pilot BOFs, three tons each.

The conclusions were that high carbon (>5%) was required, in order to have a high Cr yield. This high carbon was too much for further treatment in an AOD unit. Another condition for high chromium yield was high temperature (>1600°C). A concern during

the pilot BOF testing was slag foaming, but alternatives to decrease it were suggested. Of course, there was a need for hot metal desiliconization and dephosphorization.

As a final conclusion of the study, two alternative process routes were proposed: one quite similar to the Japanese solution, and the other based in an electric arc furnace instead of blast furnace and hot metal pretreatment (figure 7). To our knowledge these concepts did not reach application at the British Steel plants.

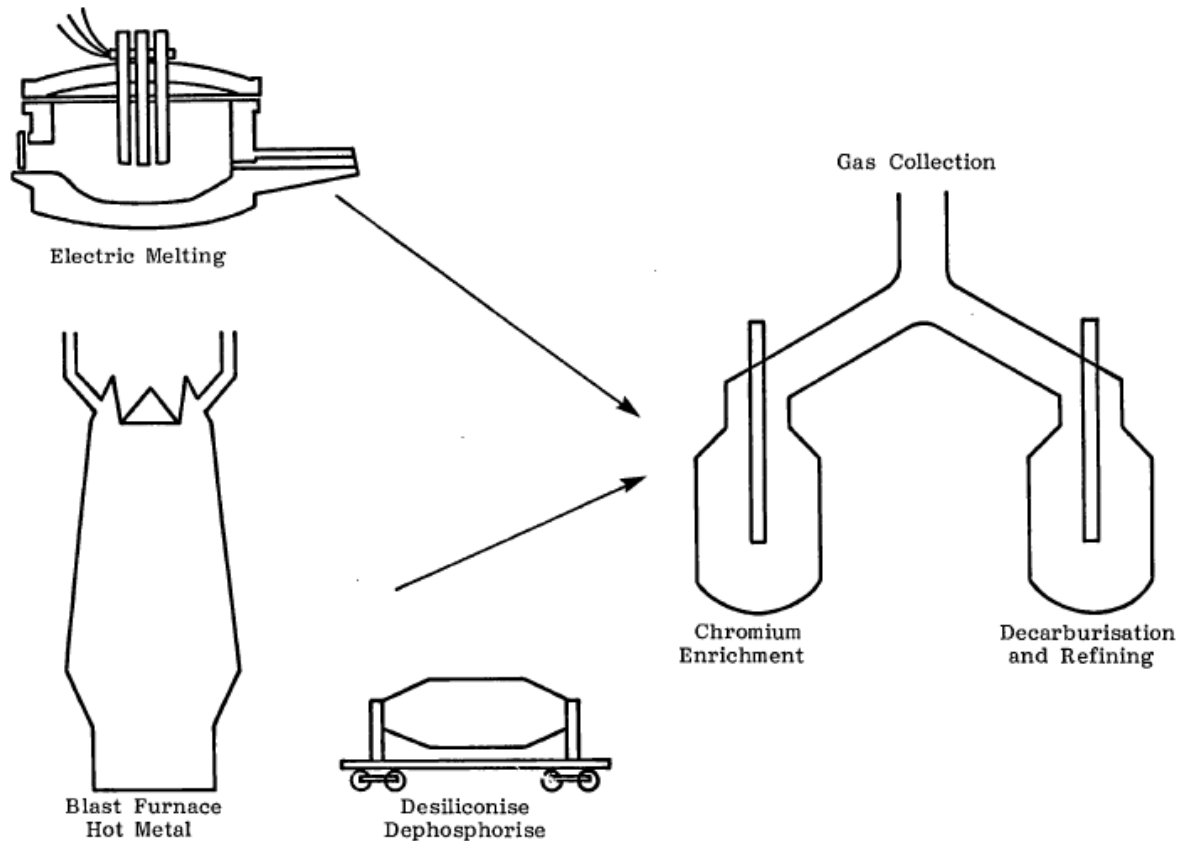


Figure 7. Outline of process for direct chromium alloying by British Steel Teeside R&D

2.3 Sweden 2012-2016. Academic research was carried out at Royal Institute of Technology, Stockholm; Lulea University of Technology, Lulea and Swerea MEFOS, Lulea. The aim was to better know the fundamentals of Chromium direct alloying in EAF, in order to give one step ahead of the previous Scandinavian success in lowering energy consumption by directly charging liquid ferrochromium to the EAF in the Tornio plant of Outokumpu (avoiding solidification, crushing and remelting), see figure 8.

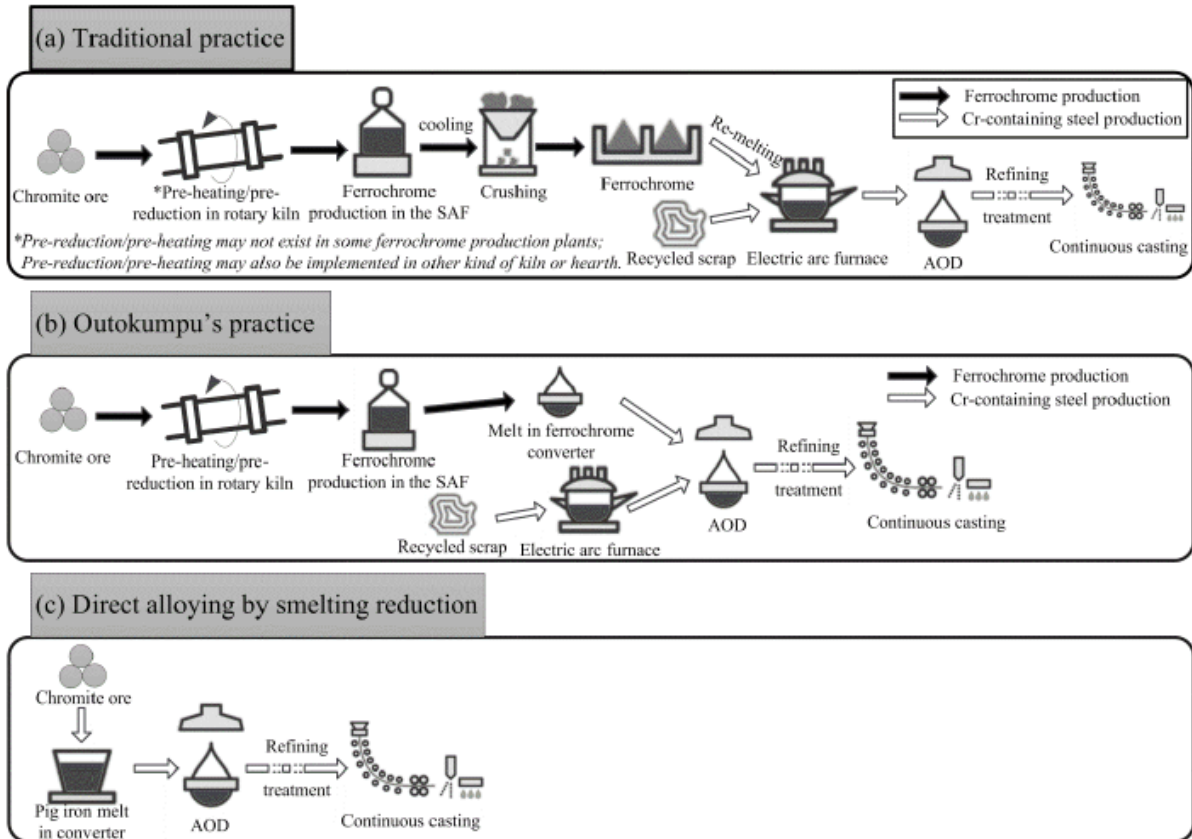


Figure 8. Traditional practice of obtaining ferrochromium and charging to the EAF for remelting (top). Practice at Outokumpu, charging molten ferrochromium directly in the AOD (middle). Purpose of the research: direct alloying with chromite ore (bottom)

The tools employed to that purpose were TGA analysis, lab induction furnace (0.1, 0.2, 0.5 kg) and induction furnace (7 and 80 kg). The investigation studied the role of iron/iron oxide and slag chemistry on reduction of chromite by graphite. Tests were carried out of reduction of chromite ore-mill scale-petroleum coke self-reducing briquettes.

2.4 Donetsk Metallurgical Plant 1987-1994. At this plant, during a long period started under the Soviet Union and then Ukraine, there was a practice of direct alloying with a mixture of chromite ore and lime in the EAF. There were two ways of preparing the mixture: mechanical mixing, or previous melting. The purpose was to obtain 0.4% Cr through ore. The yield varied between 82 and 100%.

2.5 CMRDI, Egypt – 2015. A study was brought about at this research center, aiming to use domestic low grade chromite ore for direct alloying. To this purpose, tests were carried out at a 5 kg SAF, using chromite ore, coal and mill scale. A high Cr alloy was obtained, containing 18Cr–3.7C–0.5Mn–1.5Si.

3 MANGANESE

3.1 Soviet Union 1982-1986. A development of direct alloying with manganese ore was carried out by researchers of the Donetsk Polytechnical Institute at the Azovstal steel plant. Close to 1.000.000 t of low C, Al-Si-Mn killed steel for plates, were processed with the developed process during the period

3.2 Siberian State University; KMK Relsy OOO; West Siberian Metallurgical Combine. These academic and industrial partners reported studies and industrial practice for manganese direct alloying in 2004 and 2015. The first study implied tests in a 25 t electric arc furnace, aiming to maximize replacement of silicon by low cost carbon for Mn reduction and to stabilize the recovery of manganese from the ores. The operating practice included deslagging of the oxidizing slag, then charging of low P manganese ore, placing coke breeze on the molten oxide surface (8-16% of Mn ore mass) and adding FeSi 10-15 min after coke.

A model was developed aiming to define influence of amount and timing of lime addition, slag basicity and Mn ore amount. The optimum process time length was determined, as well as the temperature range for FeSi addition. Finally, commercial practice started at WSMC for carbon and low alloyed steels, in a 25 t EAF, with an obtention of 90-95% Mn yield and 83-85% Si yield.

By 2015 a new study was carried out at the 25 t EAF, testing different briquetted mixes:

- Al-Mn-Si-Fe-C (7% Al, 25% Si, 27% Mn) – 39% Mn ore, 20% dolomite, 2% binder
- 42% FeSi45 – 41% Mn ore – 12% dolomite – 4% binder
- 17% FeSi75 – 43% Mn ore – 11% dolomite – 23% CHP ash – 5% water

The steel temperature at the moment of adding the briquettes was 1610 – 1620°C. A Mn yield of 78-88% was reported.

3.3 Mexico 2003. At the National Polytechnic Institute a research was carried out of direct alloying by MnO powder injection in a 10 kg induction furnace.

3.4 Cuba 2003-2006. At the University of Olguin, tests were realized in a 3 t induction furnace, with pirolusite Mn ore.

3.5. Georgia 2009. Academic and industrial partners joined efforts to study direct alloying by briquetting of manganese carbonate, and the development of a model for automatic control of the direct alloying process.

4. VANADIUM

4.1 Soviet Union / Russia. A long-time practice of direct alloying to recover vanadium from a vanadium converter slag was developed and practiced in late XX century. High V-Ti hot metal is produced in blast furnaces using titano-magnetite ores. Then, in the vanadium converter, a vanadium rich slag evolves as a byproduct. Reduction of V₂O₅ was carried out with FeSi and coke breeze.

The plants that did this particular direct alloying were Ural Railroad Car Plant (UVZ), Nizhni-Tagil, Magnitogorsk, Saldinskii Metallurgical Plant, Pervoural'sk Dinas Plant, Krivoi Rog, Moscow "Serp i Molot", and others.

By 2014 a theoretical study by Siberian State Industrial University of the reduction of 16% V_2O_5 vanadium converter slag was carried out. A thermodynamics assessment of reduction in a 110 t ladle with FeSi and coke fines, under nitrogen stirring (figure 9) was developed.

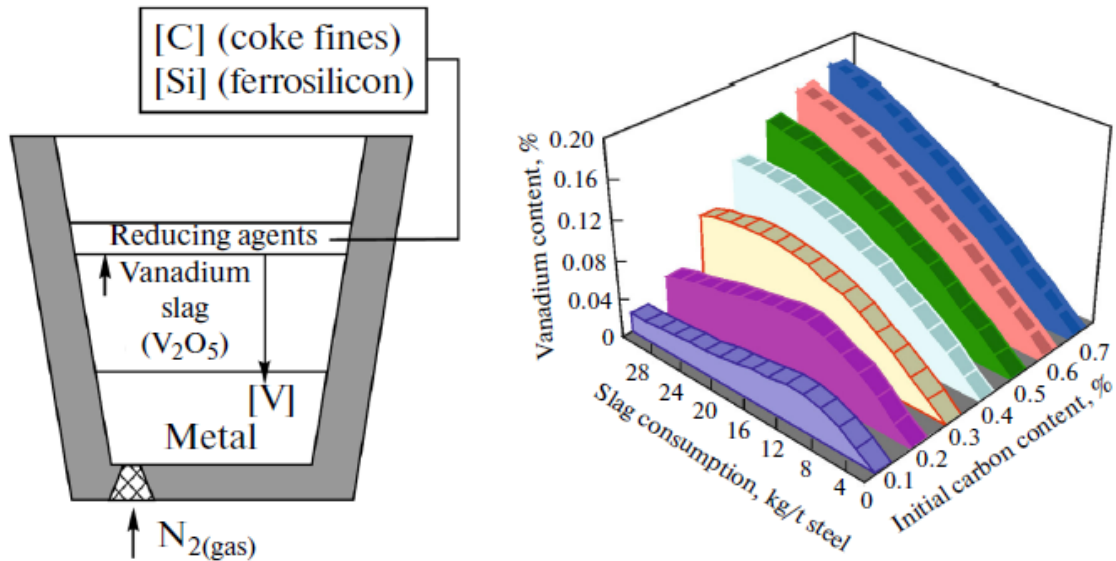


Figure 9. Left: Scheme for the thermodynamic study of direct alloying with 16% V_2O_5 slag using coke fines and FeSi as reductants, under nitrogen stirring, in a 110 t ladle. Right: Results of the study, in terms of initial carbon content, slag consumption and vanadium content.

4.2 Wuhan Univ. of Sci. & Tech. / Shijiazhuang Iron and Steel Co., China, 2014. This is a case of silico-thermic reduction of V_2O_5 . First, tests were realized in a 15 kg induction furnace using self-reducing briquettes of $V_2O_5 + FeSi + CaO + CaF_2$ in ten different recipes. The optimum briquette chemistry resulted to be 24% V_2O_5 –30% FeSi–16% CaO–30% CaF_2 , with 96% V yield.

Then industrial scale tests took place in a 60 t steel ladle, for the production of 42CrV steel (V 0.12%). The addition of the V-rich slag was practiced to the BOF stream into the ladle during tapping, at 1/3 of steel in the ladle. V yield around 96.5%. No changes in inclusions or defects were detected.

The mechanism for pre-reduction in the bath, further smelting reduction and steel – slag reduction was described as in figure 10.

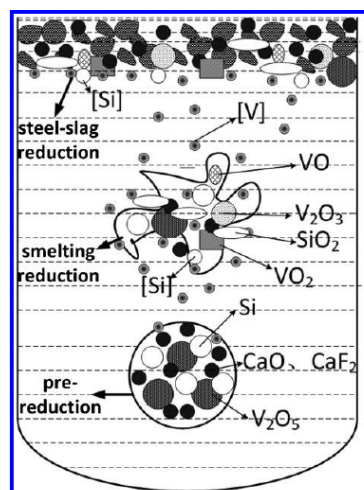


Figure 10. Mechanisms for pre-reduction, smelting reduction and steel/slag reduction for direct alloying in a steel ladle with a 16% V slag and FeSi

5. DISCUSSION

Direct alloying is a field which displays a rather small but growing activity. This activity is mostly concentrated in very few countries: Russia, Japan, Sweden and China. While in Russia, Japan and China there is industrial use of the technique, in Sweden the activity is academic. The elements attractive for direct alloying are also limited: most of the activity is around chromium, manganese, vanadium and molybdenum. The steel grades affected have been carbon steels, low alloyed, stainless and tool steel. The last decade has been the more active one, regarding publications.

Fundamentals of the direct alloying are quite similar to those for ferroalloys production, as in most cases carbothermic reduction is used. Silicothermic reduction has a secondary role. Kinetics is very important, in order to not affect productivity.

The vessels that are in use for direct alloying differ from one case to another: a bottom-blowing converter, electric arc furnaces, steel ladles. Reductants in use are coal fines, coke lumps, and carbon dissolved in hot metal. For silicon reduction, ferrosilicon has been the choice. The element for direct alloying are mostly ores (oxides, and carbonates), but in some cases, slags rich in a given element are the choice, as for vanadium. The ores may have some pre reduction step in rotary kilns, and/or agglomeration as pellets or briquettes (self-reducing in some cases), or in case of sands may be injected in the direct alloying vessel. For different purposes, lime-based slags are an important part of the metallurgy of direct alloying.

6. CONCLUSIONS

Direct alloying have had some attraction due to lower total energy consumption and CO₂ generation, and in very specific cases, lower cost. On the other hand, direct alloying complicates the steelmaking operation and increases the quantities of energy and materials, as well as the slag volume. In a few cases, carbothermic production of ferroalloys is replaced by more expensive silicothermic method.

Despite its drawbacks, direct alloying is used in some countries, for a set of specific conditions

- ✦ Japan, for chromite ore sand smelting in stainless steel production (JFE Steel Chiba No. 4)
- ✦ Russia, for Mn and Cr addition to low carbon low alloyed steels, and V recovery from converter slag

Recent R&D efforts have been aimed towards fundamentals and application of direct alloying, as in China for Cr, V, and W and in Sweden for Mo.

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