

## CLEAN STEELS FOR FUSION - D. S. Gelles, (Pacific Northwest Laboratory)\*

### OBJECTIVE

The objective of this work is to incorporate clean steel technological development into reduced activation ferritic alloy development efforts.

### SUMMARY

A summary of the workshop Clean Steels - Super Clean Steels is provided and a paper given at the Workshop entitled Clean Steels for Fusion is reproduced. The workshop demonstrated, based on ten years of steelmaking practise, that control of minor impurities P, Sb, Sn and As along with Mn and Si could effectively eliminate temper embrittlement in 3.5NiCrMoV rotor steels.

### PROGRESS AND STATUS

#### Introduction

This report is in two sections: a summary of the workshop Clean Steels - Super Clean Steels and reproduction of the paper Clean Steels for Fusion, presented at the workshop.

#### I. CLEAN STEELS SUPERCLEAN STEELS Workshop

The workshop CLEAN STEELS SUPERCLEAN STEELS organized by the Institute of Materials on behalf of the Electric Power Research Institute (EPRI) is the fifth in a series. The previous workshops were held in July 1986, July 1987, June 1988 and August 1989 in Kapfenberg, Dusseldorf, Dusseldorf, and Sapporo, respectively. The concern is temper embrittlement arising from in-service temperature conditions for large rotor shafts used in the Power Generation Industry. The adverse effects of impurity elements phosphorus (P), antimony (Sb), tin (Sn), arsenic (As), sulfur (S), oxygen (O), and deoxidants aluminum (Al) and silicon (Si) on the mechanical properties of steels have been known for many decades. P, Sb, Sn, and As, interacting with Si and Mn, cause temper embrittlement and lead to reduction in the fracture toughness ( $K^{IC}$ ) and increase in the ductile-brittle transition temperature as measured by fracture appearance (FATT). The presence of sulfide inclusions, and nonmetallic inclusions containing Al and Si can facilitate cavity nucleation at the grain boundaries and in the grains, thus facilitating creep fracture at high temperatures and ductile fractures in the upper shelf region. These changes result in reduced creep ductility at high temperatures and reduced fracture toughness at lower temperatures.

Following the identification of the elements responsible for temper embrittlement, various semi-empirical relationships have been developed and reported in the literature, enabling the steel maker and the steel user to have a "figure of merit" in relation to temper embrittlement. These relationships are of the form:

$$(1) \quad "J" = (Mn + Si) (P + Sn)$$

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$$(2) \quad "K" = (\text{Mn} + \text{Si}) (10\text{P} + 5\text{Sb} + 4\text{Sn} + \text{As})$$

$$(3) \quad "X" (\text{Broscato}) = (10\text{P} + 5\text{Sb} + 4\text{Sn} + \text{As}) / 10$$

Such values are now frequently quoted by the steel maker together with the chemical analysis. The lower the value for the figure of merit, the more resistant the steel is to temper embrittlement. In fact, an expression similar to (1) for J was used to define allowable residual element levels in early heats of low activation ferritic steels melted at Carpenter Technology for the Fusion program.  $[(\text{Mn} + \text{Si}) (\text{P} + \text{Sn} + \text{Sb}) \times 10^4 \leq 70]$ , with impurity levels in wt%

Advancements in the steel making technology during the last two decades have enabled reduction of these impurities and deoxidants to levels as low as 20 ppm leading to what might be called "clean steels". Further realization that in view of the low sulfur levels achievable, Mn is no longer necessary to 'fix' the sulfur and can, therefore, be reduced to levels as low as 0.01 to 0.02%, has resulted in "superclean steels".

The development that has made "clean" and "superclean" steels possible was secondary steel refining via ladle furnaces in conjunction with vacuum degassing in the ladle and during casting. Ladle treatment of molten steel for the purpose of desulfurization and vacuum carbon deoxidation was developed only in 1975. This provided a production means of manufacturing high purity steels that previously could only be made in the laboratory as a control for temper embrittlement research studies. The practical solution to the problem in alloy steels was to refine Mn, Si, P, Sn, As, and Sb from the steels during steel making operations. Manganese, silicon, and phosphorus are easily removed during the oxidizing stage of steel making, because they oxidize preferentially to iron, and enter the oxidizing slag. This generally is done in the electric arc furnace. Tin, arsenic, and antimony are controlled by scrap selection, with basic oxygen furnace steel scrap used as the starting material for electric arc furnace melting if possible. After separation of the oxidized steel from the oxidizing slag, it is transferred to a reducing slag in a ladle refining furnace, which removes the sulfur. Vacuum treatment of the desulfurized steel in the ladle furnace accompanied by argon bubbling provides a means for deoxidation. This leaves no oxide particles dispersed in the steel, as would be done if deoxidation were done with Si. The result is a superclean steel free of oxides and sulfides.

Several presentations were noteworthy. In his presentation at the conference, Tanaka verified the advantage of superclean steel compositions against temper embrittlement. His figure plotting values of  $\Delta\text{FATT}$  following aging at 454°C for 100,000 h as a function of the parameter J for very clean steels is shown in Figure 1. From Figure 1, it is apparent that superclean steels are insensitive to embrittlement and that the parameter J can predict low levels of embrittlement.

Nougaret showed that oxide and sulfide reduction in superclean steels also provide the benefits of improved pitting resistance and resistance to stress corrosion cracking. Tsuchiyama described complex heat treatment procedures so that a single rotor shaft forging could be used to operate both the high pressure (HP) and low pressure (LP) sections of a turbine as one unit. This required different austenitizing and tempering treatments for the shaft segments (940°C/658°C for the HP section to provide higher creep rupture strength and 910°C/650°C for the LP section to get higher toughness). The shaft was approximately 7 m long and up to 1.4 m in diameter, and a vertical electric furnace was used for heat treatment.

Also of note was a request for a show of interest in a subsequent workshop on clean steels in the 9 to 12 chrome range that would be held in 12 to 18 month, again in London. The show of interest was high.

## II. Clean Steels for Fusion

### Abstract

Fusion energy production has an inherent advantage over fission: a fuel supply with reduced long term radioactivity. One of the leading candidate materials for structural applications in a fusion reactor is a tungsten stabilized 9% chromium Martensitic steel. This alloy class is being considered because it offers the opportunity to maintain that advantage in the reactor structure as well as provide good high temperature strength and radiation induced swelling and embrittlement resistance. However, calculations indicate that to obtain acceptable radioactivity levels within 500 years after service, clean steel will be required because the niobium impurity levels must be kept below about 2 appm and nickel, molybdenum, nitrogen, copper, and aluminum must be intentionally restricted. International efforts are addressing the problems of clean steel production. Recently, a 5000 kg heat was vacuum induction melted in Japan using high purity commercial raw materials giving niobium levels less than 0.7 appm. This paper reviews the need for reduced long term radioactivity, defines the advantageous properties of the tungsten stabilized Martensitic steel class, and describes the international efforts to produce acceptable clean steels.

### Introduction

Ever since mankind has learned to duplicate the nuclear reaction controlling our sun, it has been a goal of society to harness that nuclear fusion process to create limitless quantities of energy. This goal is not yet achievable, and it is now apparent that immense finances will be needed because the machines required must be very large, and the technical problems to be overcome are very complicated. In an international effort to demonstrate the practicality of fusion energy power production, a device called the International Thermonuclear Experimental Reactor (ITER) is being designed. A recent partial assembly sketch of the ITER design is shown in Figure 2.

In the quest to procure funds for the ITER and earlier machines, it was apparent that fusion power needed to demonstrate advantages over other sources of energy. One of the inherent advantages for fusion over fission energy production is a fuel supply with reduced long term radioactivity. This was first emphasized in 1983 with the publication of the *Report of the DOE Panel on Low Activation Materials for Fusion Applications*.<sup>1</sup> The panel recommended that one of the goals of the fusion program should be a reference reactor that meets the requirements for near surface disposal of radioactive waste. The recommendation was tied to a United States regulation, 10 CFR 61,<sup>2</sup> requiring that for shallow land burial of class C waste, radioactivity levels in waste must decay to safe levels

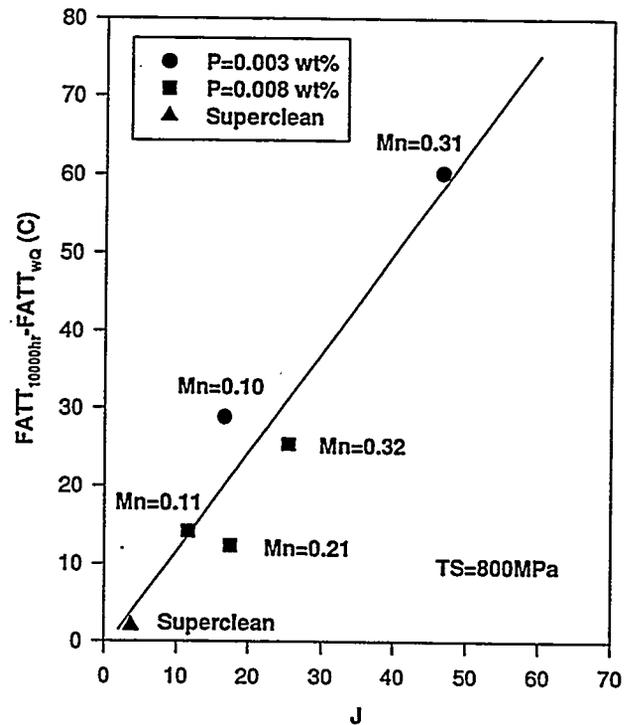


Figure 1 Embrittlement behavior in 3.5%NiCrMoV steels at low J values.

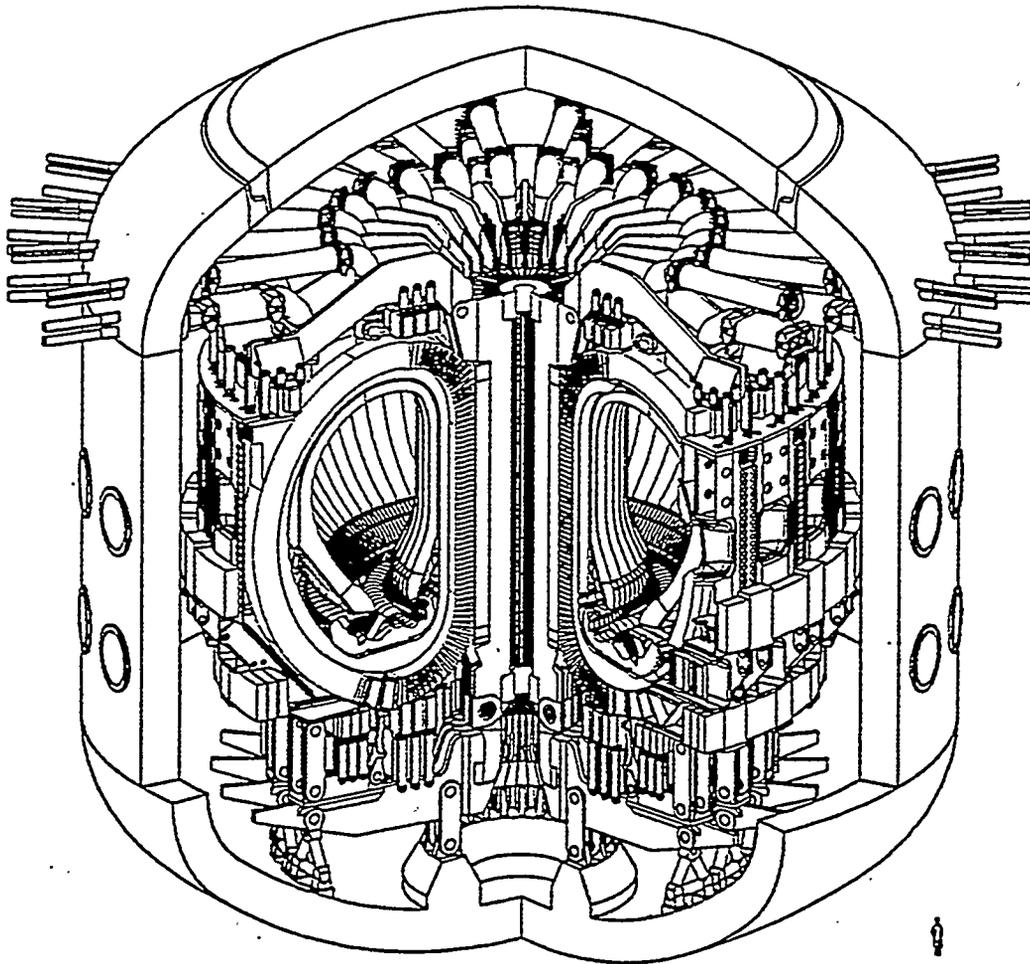


Figure 2. ITER partial assembly sketch as of July 18, 1994.

after 500 years.

To meet the requirement of safe radioactivity levels within 500 years, the panel noted that reactor components that become radioactive must not contain certain deleterious elements that produce radioactive isotopes with very long half lives. The list included nickel, nitrogen, copper, molybdenum, and niobium, but the restriction on niobium was by far the most severe: 1 atom part per million in the first wall structure. An early example of the activation level and rate of decay for an austenitic stainless steel exposed for  $9 \text{ MW}\cdot\text{y}/\text{m}^2$  in the neutron flux at a first wall of a fusion reactor is shown in Figure 3.<sup>3</sup> Activity levels vary with time as a function of the half lives for the activated isotopes and daughter products of each element shown. High levels of radioactivity are maintained in the stainless steel first wall component for very long times due to nitrogen, niobium, and molybdenum. Therefore, impurities in reactor materials had to be strictly controlled to meet such a goal.

The materials development community took this suggestion to heart in subsequent years, and efforts are now proceeding to develop reduced activation structural material versions of the following alloy classes: silicon carbide/silicon carbide composites, vanadium alloys containing chromium and titanium, and tungsten stabilized Martensitic steels. The purpose of this paper is to provide further details

concerning the development of reduced activation tungsten stabilized Martensitic steels.

### Low activation Guidelines

Since 1983, the list of elements contributing to unacceptable long term radioactivity has come under further scrutiny.<sup>4-7</sup> The criterion has been expanded to consider not only shallow land burial, but also direct handling (or "hands on" applications), and recycling of materials. The list of elements that can make an irradiated material unacceptable for shallow land burial is now considerably longer, as provided in Table 1. (Differences in the composition limits given in Table 1 are partly a measure of the assumed irradiation conditions used and partly calculational procedures.) Table 1 also includes two estimates of required

composition limits for hands on applications. However, for the purposes of steel production, niobium levels on the order of 1 wppm for disposal, or 0.01 to 0.2 wppm for hands on applications, are expected to provide the greatest restriction.

### Development of Steels for Fusion

Super 12 chrome steels are found to be viable for fusion structural applications. Interest in this alloy class first evolved from materials development for liquid metal fast fission breeder reactors, where it was shown that ferritic steels had inherent resistance to irradiation induced swelling, a process whereby materials expand in volume due to the accumulation of vacancies in internal cavities.<sup>8,9</sup> The combination of high temperature strength, good thermal conductivity, and good resistance to irradiation induced swelling and creep in these Martensitic steels has been demonstrated to provide an engineering window for fusion reactor design.<sup>10-14</sup> The high temperature limit may be restricted to temperatures as low as 450°C as a result of design specific details such as liquid lithium compatibility, but the swelling resistance of this class of materials appears to provide a stable structural material to very high irradiation doses, avoiding the need for component replacement. Precipitation of chromium rich  $\alpha'$  results in irradiation induced hardening and embrittlement,<sup>15</sup> which can be avoided by lower chromium levels in the range 7 to 9%.

Composition specifications were possible for super 12 chrome low activation steel by restricting the additions of niobium, molybdenum, nitrogen, and nickel. A large number of alloys have been designed, manufactured, and tested at laboratories around the world,<sup>16</sup> and it has been shown that tungsten can be directly substituted for molybdenum on an atom for atom basis and that tantalum can be used for niobium, providing alloys with high temperature strength on a par with 9Cr-1Mo and 12Cr-1Mo steels. Lower chromium levels avoided the need for a nickel substitute or for higher

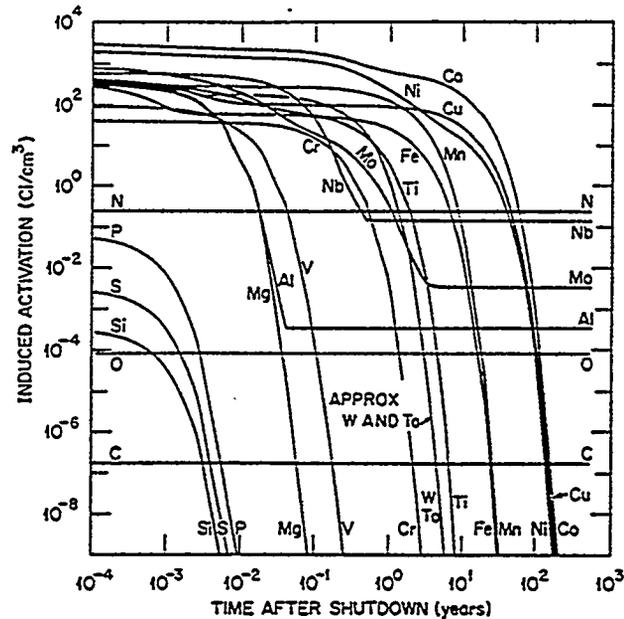


Figure 3. Induced Radioactivity in the First Wall of a Fusion Reactor Made From Austenitic Stainless Steel.<sup>3</sup>

Table 1. Low Activation Guidelines Based on Waste Disposal Criteria.

Element		Nb	Mo	Cu	N	Ni	Pb	Al	Ho	Tb	Ir	Gd	Bi	Re	Hf
Waste disposal criterion	1983 <sup>1</sup> (appm)	1	3650	2400	3650	20000									
	1984 <sup>4</sup> (wppm)	2.9	30	1200	3300	9100	31000	36000							
	1988 <sup>5</sup> (wppm)	10	500	5000	1000	20000	500000	5000	1	2	10	20	100	1000	1000
Hands on criterion	1992 <sup>6</sup> (ppm)	.18	31	651		355	900	184	.057	.021	.32	.39	.13	72	.30
	1995 <sup>7</sup> (wppm)	.0141	1.67			14800		5.24	.00608	0.0134	1.56	0.118	0.119	4.75	
Element		Se	Cd	K	Sm	Tm	Pd	Ag	Eu	Lu	Dy	Yb	Os	Co	Er
Waste disposal criterion	1988 <sup>5</sup> (wppm)	1000	2000	2000	2000	3000	5000	20000	1000	100000	3000				100
	Hands on criterion		4.9	137	.33		.72	.011	.074	.22	.54	.63	1.2	1.7	3.1
	1995 <sup>7</sup> (wppm)		2.3	1652			0.212	.00494	.585		.0048		.517	119	0.196

carbon levels to maintain a fully Martensitic structure, as well as preventing  $\alpha'$  precipitation hardening. In fact, the tungsten stabilized Martensitic steel class is found to have excellent impact resistance, with ductile to brittle transition temperatures (DBTT) below  $-60^{\circ}\text{C}$ , and excellent resistance to irradiation embrittlement.<sup>16</sup>

### Studies on Clean Steel

Two papers have addressed the question of the practicality of producing clean low activation tungsten stabilized steels.<sup>6,17</sup> Butterworth and Keown<sup>6</sup> concluded in 1991 that state of the art residual levels are generally in the range 10 to 100 ppm for high-integrity steels used for aerospace, military, and other demanding applications and therefore did not meet the more exacting requirements for hands on limits. They proposed that the route used for producing nickel-based superalloys for aerospace components where specifications were possible for some impurities to the sub-ppm level might be more successful. Careful selection of starting materials was required to exclude specific high activation elements from the feedstock.

Feasibility has in fact been demonstrated in Japan. The Nippon Kokan Corporation (NKK) has been actively developing an alloy designated F-82H for fusion reactor applications.<sup>17-20</sup> This alloy's approximate composition is Fe-8Cr-2W-0.2V-0.04Ta (in wt%) with carbon levels of about 0.1%. As part of that effort, an attempt was made to reduce the content of activating elements below the guidelines of reduced activation.<sup>17</sup> A 5000 kg ingot was vacuum induction melted from high purity commercial raw materials using commercial practices. The chemical analysis for the starting materials is given in Table 2, and the composition of the mill product is given in Table 3. Given the tight requirement needed to satisfy activation requirements, only niobium was analyzed in the raw materials. From Table 2, it can be shown that the major source of niobium is from iron and chromium, with lesser amounts from tungsten, tantalum, and vanadium. Mill product chemical analysis shows that the niobium content is quite uniform, varying from 0.5 wppm in the center to 0.07 wppm at both ends, and that silver and cobalt levels are 50 wppm. It can therefore be concluded from comparison with Table 1 that the NKK 5000 kg heat would satisfy the waste disposal criterion, but would not meet hands on criteria based on silver and niobium impurities, and cobalt levels may be too high, depending on the irradiation conditions and calculation procedures used to define the hands on low activation limit.

### Discussion

The ITER development and testing program is expected to continue well into the next century and is presently not being designed within low activation guidelines. The first commercial fusion reactor is not expected to be constructed before 2025. A commercial reactor would be expected to follow low activation guidelines, but it is not yet clear that a Martensitic steel will be selected as the structural material. Therefore, commercial production of a clean steel for fusion will not be needed in the immediate future; we have 30 years in which to develop the technology.

### Conclusions

Fusion power systems will be required to use low activation structural materials to allow shallow land burial of waste and possibly hands on or recycling options. This will mean that certain elements will be restricted from structural materials specifications. In particular, niobium must be kept below about 2 ppm for shallow land burial and 0.01 to 0.1 wppm for hands on and recycling options. A tungsten stabilized Martensitic steel appears to be a good choice for fusion structural materials applications, and therefore clean steels may be selected. However, commercial production of such steels will not be needed for another thirty years, giving ample time to advance steel making to the levels needed.

Table 2. Chemical analysis of raw materials<sup>a</sup>

Element	Raw materials	Nb [ppm]	Mass of melting [kg]	Nominal content [wt.%]	Calculated Nb content in F-82H [ppm]
C	carbonet	-	5	0.1	-
Si	metallic silicon	< 1.0	5	0.1	<0.001
Mn	metallic manganese	< 1.0	5	0.1	<0.001
Cr	high purity metallic chromium	10	385	7.7	0.15
W	metallic tungsten	2.0	100	2.0	0.04
V	metallic vanadium	10.0	10	0.2	0.02
Ta	metallic tantalum	85.0	1	0.04	0.034
Ti	sponge titanium	1.1	1	0.02	<0.0004
Fe	converter steel	<0.5	4487	bal.	<0.45
total			5000	100	<0.7

<sup>a</sup> The dash means not analyzed.

Table 3. Chemical Composition of Mill Product F-82H (wt.%).<sup>a</sup>

Impurity	Ladle	Plates			Impurity	Ladle	Plates		
		top	middle	bottom			top	middle	bottom
C	0.096	0.097	0.110	0.094	Ti	0.008	0.007	0.007	0.007
Si	0.10	0.09	0.09	0.09	Nb	<0.0005	0.00007	0.00005	0.00007
Mn	0.15	0.07	0.07	0.07	Sol.Al	0.005	0.007	0.007	0.008
P	0.003	0.002	0.003	0.003	W	2.1	2.1	2.1	2.1
S	0.003	0.0032	0.0029	0.0027	Ta	0.04	0.03	0.03	0.03
Cu	0.01	<0.01	<0.01	<0.01	B	-	0.0004	0.0003	0.0004
Ni	<0.1	0.03	0.03	0.03	T.N	0.0043	0.0043	0.0044	0.0047
Cr	7.71	7.46	7.46	7.46	T.O	0.0028	0.0033	0.0049	0.0037
Mo	<0.01	<0.001	<0.001	<0.001	Ag	-	-	<0.005	-
V	0.18	0.18	0.18	0.18	Co	-	-	0.005	-

<sup>a</sup> The dash means not analyzed.

**FUTURE WORK**

This effort will be continued only when appropriate.

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