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THE EFFECT OF MANGANESE AND SILICON CONTENT ON THE HOT WORKABILITY OF TYPE 304 STAINLESS STEEL CONTAINING 2 w/o BORON

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ABSTRACT

Increased hot workability of Type 304 stainless steel containing approximately 2 w/o boron was obtained by maintaining the manganese and silicon contents of the alloy above minimum levels of 1.40 w/o and 0.60 w/o, respectively. Close control of the range of temperatures over which hot working was carried out was also demonstrated to be of importance. However, over the range investigated variation in the temperature of hot working was of secondary significance as compared with alloy composition.

INTRODUCTION

The use of boron as a reactor control material has been of interest because of its high capture cross section for thermal neutrons. The operational problems resulting from use of boron-containing materials for control and shielding have been discussed quite extensively in the literature. This publication, however, deals only with the specific problem of incorporating significant quantities of boron in an austenitic stainless steel without reducing the hot working properties of the melted and cast alloy to such an extent that it loses all practical application in the wrought form. No complete solution to the problem has been discovered to date. Indeed, the best results to date still place austenitic stainless steels containing 2 w/o boron in a class which must be considered a difficult product to convert from a cast structure to a usable wrought product with any degree of economic practicality. The particular point which is presented herein is the fact that with reasonable control of composition and hot working conditions the difficulties can be minimized and satisfactory results obtained.

At present no attempt should be made to extrapolate those data to higher boron contents or to completely explain the results at the level presently under consideration. This must of necessity be a progress report and an attempt to stimulate additional work on alloys of this type as long as they are considered acceptable for use as control materials up to reasonable levels of burnup.

BACKGROUND

In 1932, Wasmuht[1] experimented with 18-8 stainless steel containing boron. He succeeded in producing precipitation-hardening alloys of this grade with 0.55 to 1.14% boron and about 0.15% carbon.

In 1957, the results of work carried out in England by T. H. Middleham and associates[2] was published, indicating success in forging Fe-B-Al alloys containing up to 4.75 w/o boron. The success is attributed to a shift in the eutectic composition, resulting in a decrease in the size as well as amount of the hard phase present. An increase in solid solubility seems to be ruled out, since no significant structural change was obtained with quenching or annealing.

Almost all work carried on in this country dealing with boron-bearing steels has been concerned with relatively small additions of boron for the purpose of improving hardenability, conserving strategic materials, and more recently in the field of high-temperature alloys. In none of these applications does the boron content approach the level which is deemed necessary for satisfactory use as a reactor control material. The aforementioned uses of boron have been, in almost all cases, restricted to levels below 0.003 w/o, although some experimental high-temperature alloys have been compounded with as much as 1 w/o boron. In the case of one of these alloys, cobalt-base S-816, boron contents over 0.15 w/o render the material unforgeable and uses are limited to cast products.[3]

The physical metallurgy of low boron-iron base alloys and the basic $Fe-Fe_2B$ system have been covered in great length, and in spite of many as yet unresolved inconsistencies the use of boron in small amounts as an alloying element in steels has been generally accepted. The study of boron as a major alloying element has so far been restricted primarily to the nuclear industry. A fair amount of Type 304 stainless steel with up to 2 w/o boron has been produced and is in use. However, there apparently has been no detailed study of the effects of adding boron at this level, or of possible methods of further modifying the stainless alloy to obtain a more easily handled product. Though produced commercially, the material still must be considered to be in the experimental stage with respect to producing a wrought product.

Boron has a very low solubility in both α and γ iron. Also, the complex borides formed with Fe, Ni, Cr, and C in commercial alloys impart a condition of extreme hot shortness in the range of normal working temperatures. This is attributed to the presence of the hard boride phase as well as eutectic melting encountered at these temperatures. Significant intergranular melting has been observed as low as 1175°C in both cobalt- and iron-base alloys containing boron.[4] The NiB system exhibits a eutectic at about

1080°C,[5] whereas the Fe-B eutectic temperature is about 1175°C. Cr-Ni stainless steels containing only 0.50 w/o B exhibit detrimental eutectic melting above 1200°C. At this level of boron content, hot-working characteristics improve as the carbon content is decreased.[6]

CURRENT WORK

Interest at ANL in the practical aspects of hot working the boron-bearing Type 304 was heightened when several ingots proved to be completely unmanageable after sufficient success in fabrication of the alloy had been achieved to warrant its use in the Experimental Boiling Water Reactor.

A cursory examination indicated that a readily apparent reason existed for the poor performance of these ingots. As shown in Table I, the presence of manganese and silicon at a level normally associated with residual analysis is the property which sets the two low yield ingots apart from the balance of the material. An additional 18 ingots supplied by commercial fabricators to a commercial nuclear power organization revealed the same relationship. Two heats with silicon contents of 0.10 w/o and normal manganese (1.60 w/o) were associated with very low yields.

Table I

CHEMICAL COMPOSITIONS AND YIELDS OF COMMERCIAL VACUUM MELTED 2 w/o BORON TYPE 304 STAINLESS STEEL INGOTS

Heat	Yield, %	Analysis, Weight Per Cent								
		C	Mn	P	S	Si	Cr	Ni	B	N
1	Very Low	0.02	0.10	-	0.011	0.08	18.97	9.60	2.00	-
2	0	0.05	0.06	-	0.015	0.18	19.06	9.38	1.92	0.006[a]
3	50	0.07	1.47	0.013	0.004	0.53	18.82	8.70	2.02	-
4	50	0.05	1.81	0.009	0.014	0.47	18.33	9.60	2.02	-
5	50	0.05	1.66	0.011	0.011	0.56	19.06	9.92	1.91	-
6	50[b]	0.02	1.65	0.008	0.016	0.46	18.90	9.46	2.01	-
7	50	0.05	1.63	0.008	0.002	0.54	18.48	9.46	2.13	-
8	50	0.02	1.17	0.017	0.012	0.55	17.54	9.60	2.08	-

[a]ANL analysis.
[b]Yield low due to pouring problems.

Subsequent remelting of the commercial scrap at ANL with appropriate additions of manganese and silicon to obtain analyses more typical of commercial Type 304 resulted in satisfactory hot-working properties. "Satisfactory" does not imply ease of working. Compared to structural or low alloy steels and most of the austenitic stainless steels, the hot working of 2 w/o boron stainless steel must still be considered a critical operation requiring careful control of operating practices.

The Effect of Variation in Composition on Hot Workability

Four small ingots were vacuum melted from the commercial scrap with alloy additions, and the resultant compositions are indicated in Table II. Ingot No. 1 was a remelt of the commercial scrap with no additions, and served as a control.

Table II

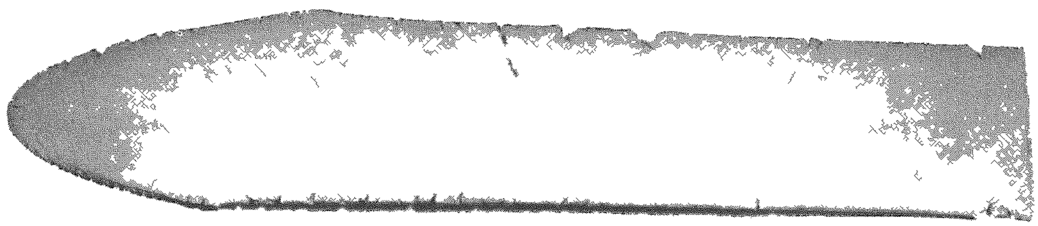
CHEMICAL COMPOSITIONS OF ANL VACUUM MELTED EXPERIMENTAL INGOTS

Ingot No.	Analysis, Weight Per Cent							
	C	Mn	S	Si	Cr	Ni	B	N
X	0.05	1.40	0.017	0.68	18.69	9.33	2.19	0.021
1	0.03	0.09	0.010	0.10	18.97	9.45	2.29	0.014
2	0.03	1.45	0.020	0.10	18.79	9.30	2.44	0.013
3	0.02	1.53	0.021	0.11	18.71	9.35	2.36	0.020

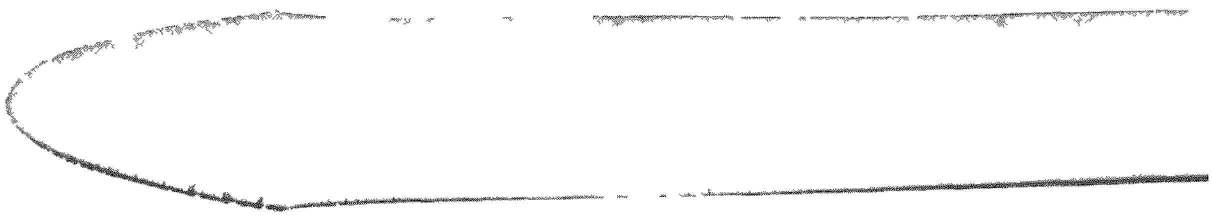
The relative hot workability of the ingots, as measured by the amount of edge cracking resulting on conversion from a 2 x 4-in. cross section to $\frac{1}{8}$-in.-thick strip is indicated in Figure 1. Edge cracking and tearing to a depth of one inch is apparent in the product of ingot No. 1, the low-Mn, low-Si ingot. The product of this ingot was extremely magnetic. The product of ingot X was very good, exhibiting virtually no edge cracking. This material was slightly magnetic. The strip rolled from ingot No. 3 (normal Mn, low Si) contained some edge cracks and was only slightly improved over the original analysis. This product was nonmagnetic.

No product was obtained from ingot No. 2. The billet broke up early in the rolling. This ingot had virtually the same analysis as ingot No. 3. The only difference in the two was that ingot No. 3 was melted with nitrogen-bearing electrolytic manganese and the electrolytic manganese used for ingot No. 2 contained no nitrogen. However, there does not appear to be enough difference in the nitrogen levels of the product to account for the difference in hot workability, nor is there sufficient evidence to indicate that nitrogen in itself in this amount would improve the hot workability.

Ingot No. 1-.03% C; 09% Mn, 10% Si



Ingot No. 3-.03% C, I 45% Mn, 10% Si



Ingot No X- 05% C, I 40% Mn, 68% Si

Figure 1. The Effect of Variation in Alloy Composition of Edge Cracking Observed in Strip Rolled from Type 304 Stainless Steel Containing 2 w/o Boron

The overall results tend to indicate that both the Mn and Si should be above a given minimum to yield the best hot-working properties. This could be associated with the degree and type of deoxidation employed and the presence and properties of delta ferrite at the rolling temperatures.

The commercial heats encountered had indicated that the product of high-yield ingots was nonmagnetic whereas the product of the poor ingots was strongly magnetic. As indicated earlier, the best laboratory ingot produced was slightly magnetic. The presence of significant amounts of delta ferrite, resulting in a duplex structure at elevated temperatures, is known to reduce the hot workability of the austenitic stainless steels. It is postulated that the presence of a significant amount of delta ferrite at hot-working temperatures contributes greatly to the lack of hot workability of this alloy. The presence of the hard, brittle boride phase reduces the amount of delta ferrite necessary to result in gross detrimental effects.

Although increased silicon contents tend to result in more delta ferrite, the silicon appears to be necessary for hot ductility. This may be a result of the effect of increased silicon on the properties of any delta ferrite present as well as its effect on the composition of nonmetallic inclusions. The stiffening effect of the silicon on delta ferrite may make it more compatible with the boride phase.

The presence of the delta ferrite may be only a secondary factor in view of the brittle borides and possibilities of eutectic melting. The fact that increased nickel contents seem to have no great effect whereas the manganese content appears to be highly significant indicates that the major problem may not be the presence of austenite stabilizers, but merely the need for manganese to reduce hot shortness resulting from the presence of FeS. However, at this stage the observed difference in the rollability of magnetic and nonmagnetic material makes the effect of the high-temperature ferrite worthy of study.

The Effect of Temperature on Hot Workability

The effect of soaking temperature on the hot workability of the various compositions was appraised by use of a hot upset test. In this test, small cylinders, $\frac{1}{2}$ in. in diameter and $1\frac{1}{4}$ in. long, were machined from a portion of the as-cast product and upset various amounts over a range of temperatures.

At its best, this test is only qualitative and often contradictory. When possible, the hot upset test should be replaced by a hot twist test to determine the ability of the material to withstand hot plastic deformation and the force required to perform the hot work.

As indicated in Figure 2, ingots X, 1, and 3 all displayed almost a complete lack of good forgeability characteristics as measured by the hot upset test. Those samples which were upset after soaking at 1165°C did not show a great decrease in forgeability due to anticipated eutectic melting. In fact, all soaking temperatures between 1065°C and 1165°C seemed to produce the same result.

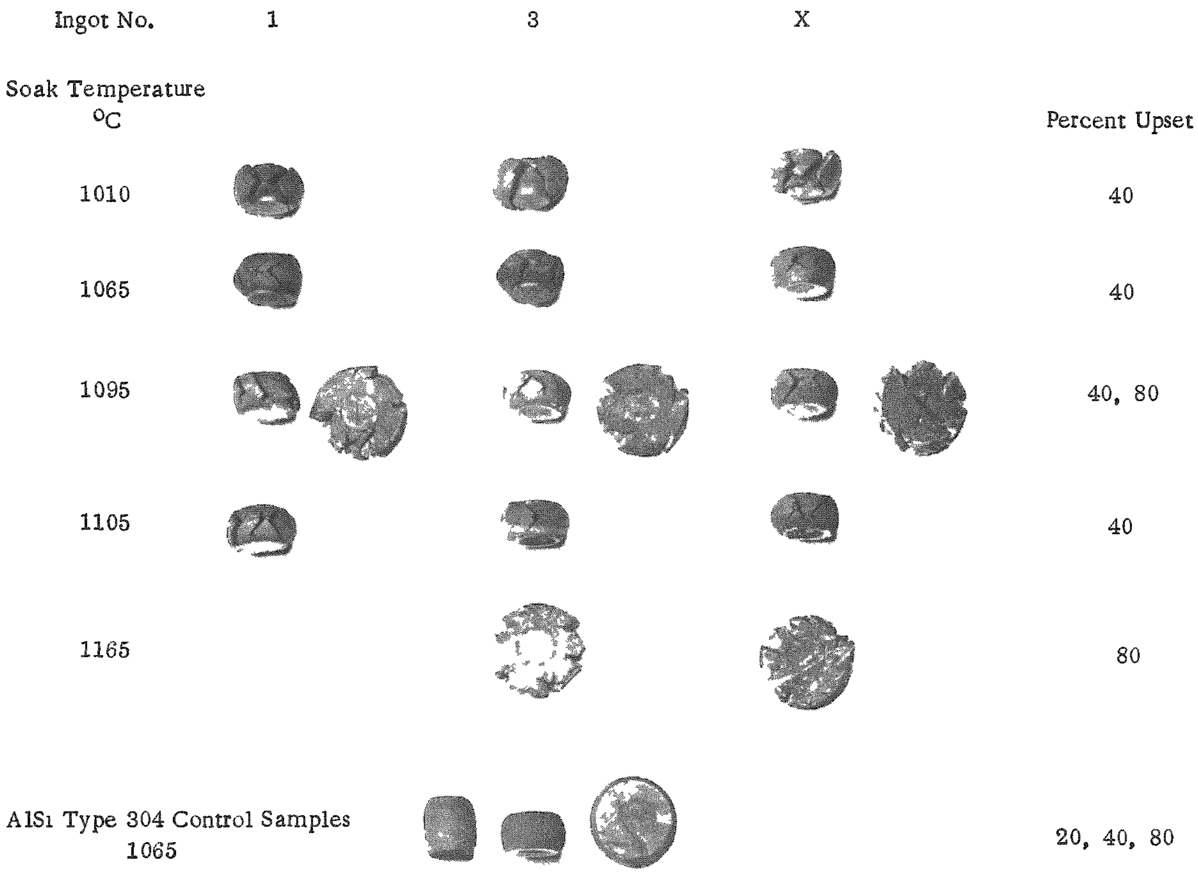
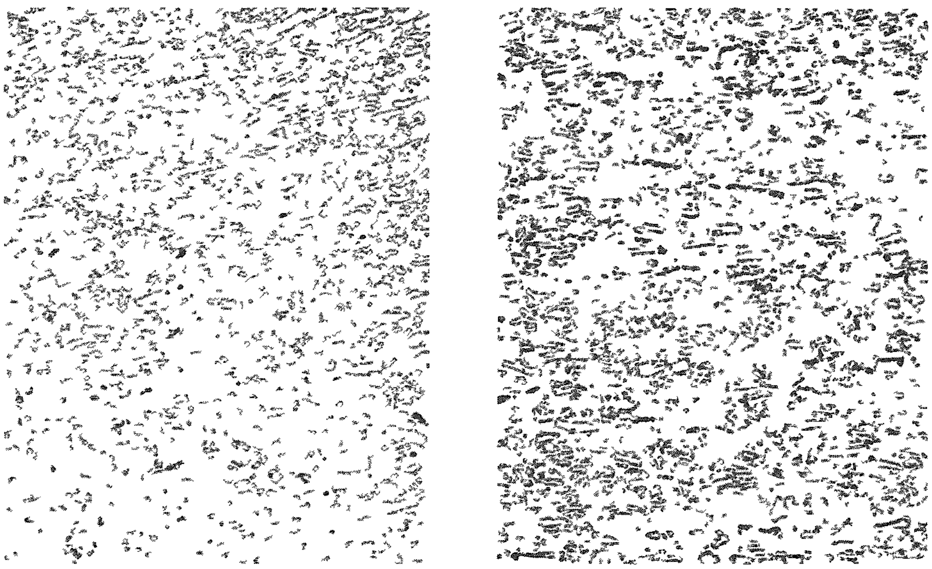


Figure 2. Result of Hot Upset Testing Samples of Various Alloy Compositions Over a Range of Temperatures from 1010°-1165°C. Side View is Shown of 40% Upset Samples, Top View is Shown of 80% Upset Samples.

Metallographic study of samples heated at 1160°C and water quenched showed no evidence of intergranular melting. However, based on information on the known eutectic temperatures, and the possibility of undetected effects of the increased temperature, the hot working of experimental ingots was controlled to provide a maximum soak temperature of 1105°C and a hot working range from 1040°C to 1095°C.

As illustrated in Figure 3, the microstructure of the as-cast and the as-rolled, annealed and water-quenched samples of the workable and unworkable compositions give no apparent indication of a reason for the difference in hot workability.



(a) (b)

Figure 3. Hot Rolled, Annealed and Water Quenched Microstructure of 2% Boron Type 304 Stainless Steel. (a) High yield material - 1.40% Mn, 0.68% Si; (b) Low yield material - 0.09% Mn, 0.10% Si. Original Mag. 250X, etched with Marbles Reagent.

SUMMARY

Based on the results of commercial heats and those achieved with the laboratory ingots it appears desirable to specify that the manganese content of the 2 w/o boron Type 304 stainless steel be a minimum of 1.50%. Likewise, a minimum content of 0.50% silicon is now specified by ANL. Because of the possibility of excessive intergranular melting at relatively low temperatures, limiting the maximum soaking temperature for ingots of this grade is also indicated. Further studies of the hot working of this alloy appear to be in order as long as it is considered a worthwhile control material.

In the realm of prognostication, the study of the effect of increasing the nitrogen content of the alloy may be rewarding. If more of the boron can be maintained in the product as BN, a form known to be ineffectual with respect to hardenability, a decrease in the observed hot shortness may result. The dispersion of fine particles of BN might prove to reduce the amount and particle size of the complex iron-boride eutectic present. At the same time, the presence of dissolved nitrogen should provide increased austenite stability at hot-working temperatures.

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