ELEVATED TEMPERATURE TENSILE PROPERTIES of BORATED 304 STAINLESS STEEL: EFFECT of BORIDE DISPERSION on STRENGTH and DUCTILITY*

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INTRODUCTION

Conventional cast and wrought ("Ingot Metallurgy") borated 304 stainless steel has been used for a number of years in spent fuel storage applications where a combination of structural integrity and neutron criticality control are required. Similar requirements apply for materials used in transport cask baskets, and borated stainless steel is, in fact, an attractive material for such applications. However, in the high boron contents (>1.0 wt.%) which are most useful for criticality control, the conventional cast and wrought material suffers from low ductility as well as low impact toughness. The microstructural reason for these poor properties is the relatively coarse size of the boride particles in these alloys, which act as sites for crack initiation.

Recently, a "premium" grade of borated 304 stainless steel has been introduced (Strobel and Smith, 1988) which is made by a Powder Metallurgy (PM) process. This material has greatly improved ductility and impact properties relative to the conventional cast and wrought product. In addition, an ASTM specification has been developed for borated stainless steel. This specification (ASTM A887) contains 8 different material Types with respect to boron content - with the highest level (Type B7) having permissible range from 1.75 to 2.25 wt. % boron - and each Type contains two different Grades of material based on tensile and impact properties. While the ASTM specification is properties-based and does not require a specific production process for a particular grade of material, the PM material qualifies as "Grade A" material while the conventional Ingot Metallurgy (IM) material generally qualifies as "Grade B" material.

This paper presents a comparison of the tensile properties of PM "Grade A" material with that of the conventional IM "Grade B" material for two selected Types (i.e., boron contents) as defined by the ASTM A887 specification: Types 304B5 and 304B7. Tensile properties have been generated for these materials at temperatures ranging from room temperature to 400°C (752°F). The data at higher temperatures are required for ASME Code Case purposes, since the use temperature of a basket under "worst case" cask conditions may be as high as 343°C (650°F), due to self-heating by the activated fuel elements. We will also discuss the current status of efforts aimed at obtaining an ASME Boiler and Pressure Vessel Code Case for selected grades of borated stainless steel covered by the ASTM A887 specification.

*This work conducted at Sandia National Laboratories, supported by the U. S. Department of Energy under contract number DE-AC04-76DP00789.

MATERIALS CHARACTERIZATION AND TESTING PROCEDURES

The SNL study (Stephens and Sorenson 1990) was designed to first examine the high boron content types (boron content >1 wt.%) in ASTM A887, i.e., the Types designated as 304B4, 304B5, 304B6 and 304B7 - since these types are the most useful for criticality control applications. For these high-boron Types, only the Grade A material appears to have adequate impact properties to permit inclusion in the ASME code case inquiry - based on the impact requirements shown in ASTM A887. In fact, the highest boron-bearing Grade B material with somewhat acceptable impact properties is Type 304B2 Grade B, which has a permissible boron content range of 0.50-0.75 wt.% and a required minimum Charpy V-Notch Energy of 22 Joules (16 ft-lbs). All four heats of material discussed in this paper - i.e., Type 304B5 Grades A and B, along with Type 304B7 Grades A and B - were produced and supplied by Carpenter Technology Corporation, the chemical analyses performed by Carpenter to certify conformance with ASTM A887 are shown in Table 1. All material was tested at SNL in the solution annealed condition.

Table 1. Chemical composition (in wt.%), heat number information and other required properties for the four different lots of borated stainless steel studied. Note the compact labels used for each lot of material in the remainder of this paper, and that the impact properties of both 304B5B and 304B7B are so low as to not have a required minimum value in ASTM A887.

Element	304B5, Grade A ("304B5A")	304B5, Grade B ("304B5B")	304B7, Grade A ("304B7A")	304B7, Grade B ("304B7B")
Carbon	0.032	0.034	0.027	0.034
Manganese	1.83	1.93	1.74	1.79
Phosphorus	0.014	0.014	0.024	0.022
Sulfur	0.002	0.001	0.004	0.004
Molybdenum	0.02	0.03	0.29	0.28
Copper	0.04	0.04	0.10	0.12
Cobalt	0.06	0.06	-----	0.22
Silicon	0.73	0.71	0.58	0.67
Chromium	18.39	18.22	18.40	18.00
Nickel	12.98	13.03	13.01	13.42
Boron	1.41	1.38	2.19	1.90
Iron	Balance	Balance	Balance	Balance
Heat #	C1835	11666	C1592	94480
Required Min. Elongation (%)	24.0	13.0	17.0	6.0
Required Min. Charpy V-Notch Energy - J(ft-lbs)	31(23)	-----	14(10)	-----

Previous X-ray diffraction results generated at our laboratory have indicated that virtually all of the boron is present in these materials as precipitates of either Cr_2B or as $(Cr,Fe)_2B$. This is because the solubility of boron in both 18Cr-15Ni and 20Cr-25Ni stainless steels is <0.001 wt.% at 600°C (Goldschmidt 1979) - boron would be expected to have a similar solubility in the alloys in the present study. Rolling plane cross sections were prepared from each lot of material and were examined using both scanning electron microscopy (backscattered electron images) and quantitative image analysis to characterize the boride dispersion. Figure 1 shows representative areas from each of the four lots of material. The boride phase is consistently finer in the PM-processed Grade A material compared to the IM-processed Grade B material. Close inspection of the Grade B material shown in Figures 1b and 1d also indicates the presence of cracks in some of the larger boride particles. The area of roughly 1000 particles from each material were obtained from BSE images, and the size distribution of these areas are plotted

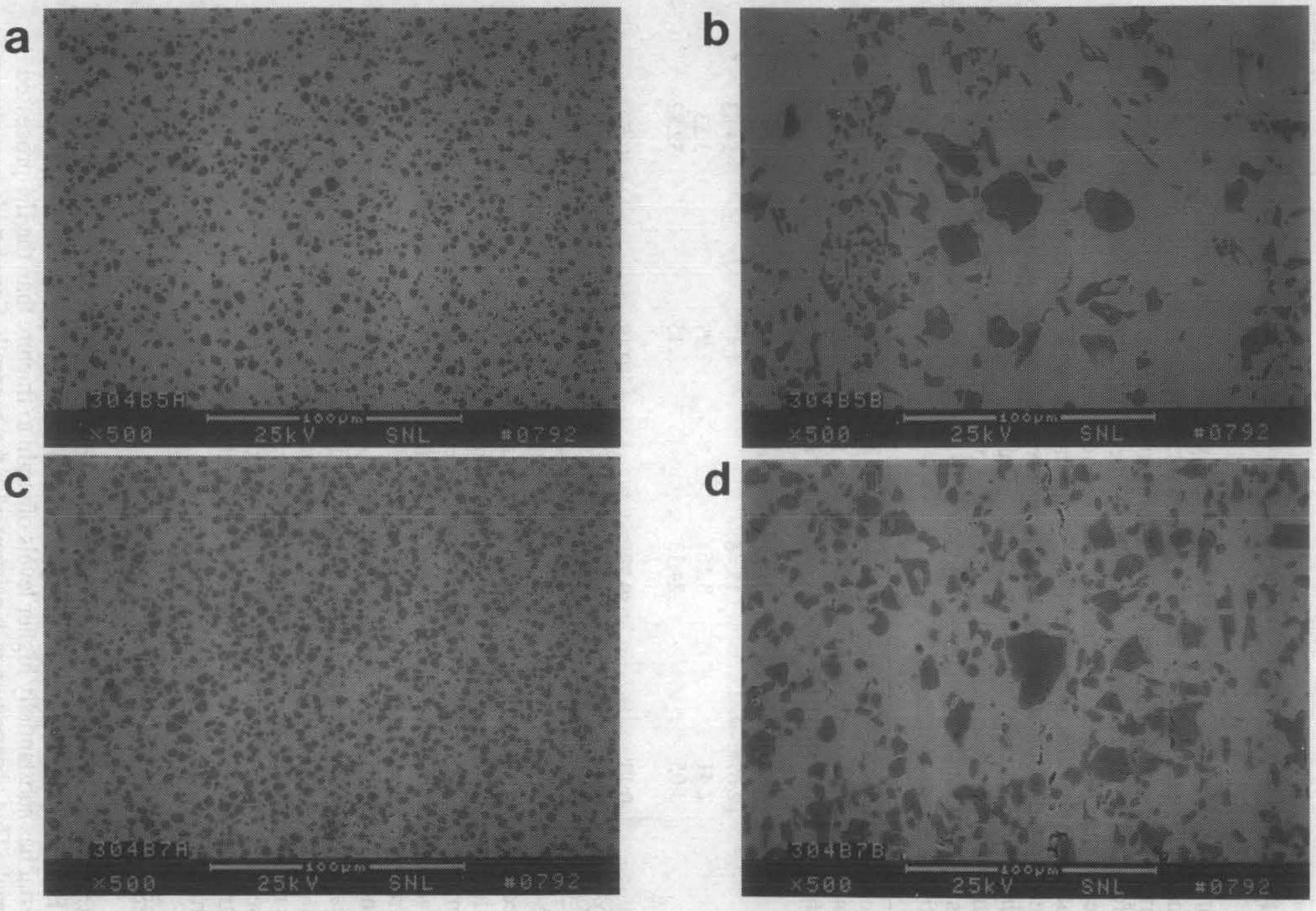


Figure 1. Backscattered electron micrographs (with atomic number contrast) obtained at an original magnification of 500x. The boride particles - either Cr_2B or as $(Cr,Fe)_2B$ - show up darker than the austenitic matrix due to their lower average atomic number. Roll direction is parallel to the short dimension of each photo. (a) 304B5A. (b) 304B5B. (c) 304B7A. (d) 304B7B.

using a log scale in Figure 2. The log scale is needed since the distribution of boride sizes in each lot of material is quite broad, spanning at least 2 orders of magnitude in area. For each lot of material, the area size distribution, $Y(x(\mu m^2))$, is well approximated by the log-normal distribution (Dixon and Massey 1957)

$$Y(x\ (\mu m^2)) = (1/(\ln \sigma\ (2\pi)^{1/2}))\ (\exp [-0.5((\ln x\ (\mu m^2) - \ln \mu\ (\mu m^2))/\ln \sigma)^2] \qquad (1)$$

where $\ln \mu\ (\mu m^2)$ and $\ln \sigma$ are known as the mean and variance of the distribution, respectively. The log-normal fit for each lot of material is plotted as a straight line in Figure 2. The log-normal parameters, as well as the average (first moment of eq.(1)), minimum and maximum boride areas for each lot of material are shown in Table 2. Whether one uses the average area or maximum area as the basis of statistical measure, the boride particles in the Grade A, PM-processed material are significantly finer than for the case of the Grade B, IM-processed material. There is no doubt that the largest particles present are most problematic with respect to limiting toughness and ductility in these materials. Thus, the fact that both Grade A materials have maximum boride particle areas roughly an order of magnitude smaller than their Grade B counterparts suggests that their toughness and ductility should be substantially improved relative to the properties of Grade B material.

Table 2. Log-normal distribution parameters and other area size information for each lot of material studied. Area size information obtained from rolling plane samples. The average area, denoted as <A>, for each lot is obtained from the *first* moment of the log-normal equation, and is equal to $\exp [\ln \mu + 0.5^* \ln^2 \sigma]$.

Item	304B5A	304B5B	304B7A	304B7B
$\mu\ (\mu m^2)$	2.07	12.46	4.47	14.83
$\sigma\ (\mu m^2)$	2.41	3.16	2.99	3.53
<A> (μm^2)	3.05	24.13	8.15	32.82
min. area (μm^2)	0.13	0.77	0.18	0.5
max. area (μm^2)	20.0	456.	69.7	597.

Round tensile specimens with a 3/8"-24 thread, 1/4" gage diameter and 1" long gage section were machined from both 304B5A and 304B5B material. Flat plate specimens were machined with a 1/2" wide gage, 2" long gage section and nominal thickness of 0.200" for the 304B7A and 304B7B materials. The majority of the samples were tested at all temperatures in the transverse direction; longitudinal samples were also tested both at room temperature and 400°C (752°F). In order to collect complete strength and ductility data, all tensile tests were run at a constant engineering strain rate to fracture. For 304B5A, 304B5B and 304B7A material, the majority of tests were performed at an engineering strain rate of 5%/min., while for 304B7B material, most testing was done at 0.5%/min. Additional tensile data for 304B5A and 304B7A samples were obtained at 0.5 and 50%/min. and temperatures of 23°C (73°F) and 400°C (752°F): these tests did *not* indicate any strain-rate sensitivity over this strain rate/temperature range. Similarly, 23°C (73°F) tests of 304B7B material run at 5%/min. showed no difference in properties compared with tests run at 0.5%/min.

TENSILE TEST RESULTS AND DISCUSSION

The strain to fracture as a function of temperature for both Grades of 304B5 and 304B7 material are shown in Figures 3a and 3b, respectively. For both material Types, the PM-processed Grade A material has substantially higher levels of strain to fracture than the IM-processed Grade B material. This observation is consistent with the generally finer boride particle size in the PM-processed material compared to IM-processed material. Within a particular Grade of material (A or B), increased boron content tends to reduce ductility. Regression analysis of the

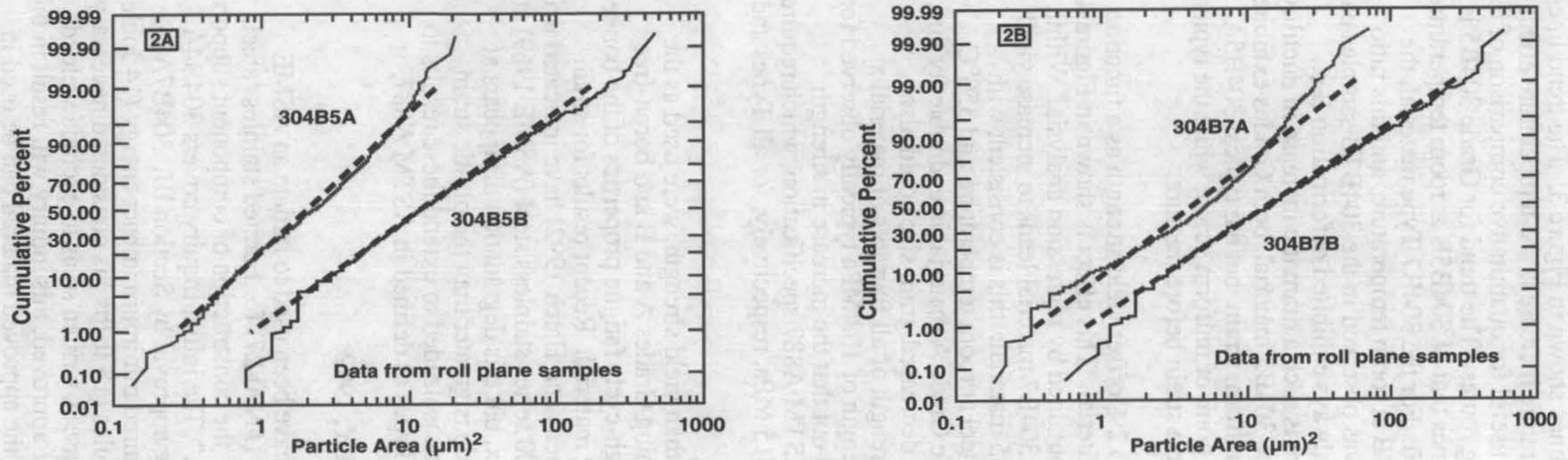


Figure 2. Area size distributions of boride particles plotted on logarithmic probability paper, where a straight line represents a log-normal size distribution. The lines from 1 to 99% represent the best fit log-normal distribution obtained by regression analysis. (a) 304B5A and 304B5B. (b) 304B7A and 304B7A.

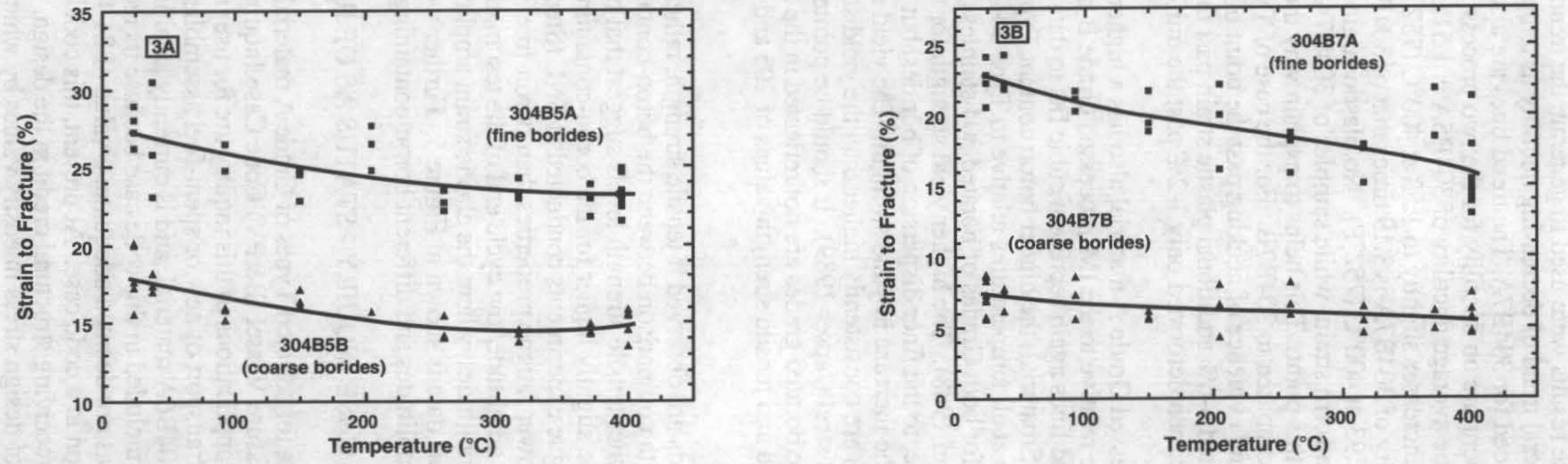


Figure 3. Strain-to-fracture as a function of temperature for all four lots of material studied in this paper. The trend lines drawn were obtained from regression analysis using a cubic equation. (a) 304B5A and 304B5B material. (b) 304B7A and 304B7B material.

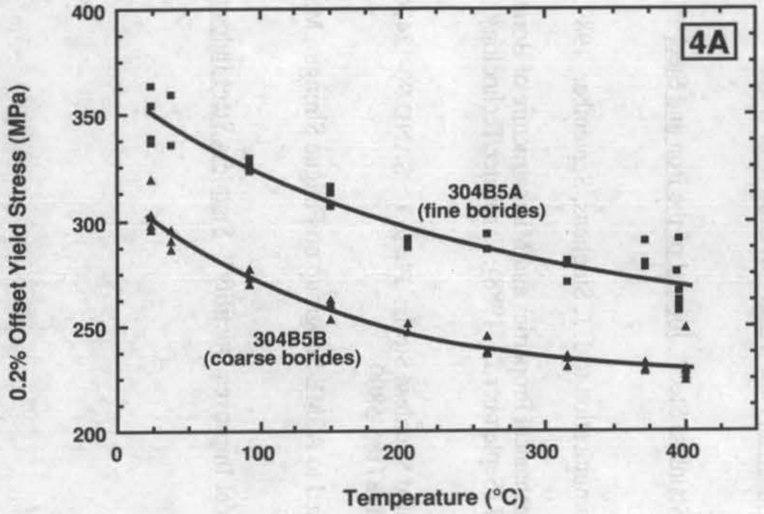
strain to fracture vs. temperature data was performed for each material lot using a cubic equation; these results were used to generate the trend lines shown in Figure 3. The trend lines indicate a general trend of decreasing ductility as temperature increases: the temperature effect is most pronounced for 304B7A. The trend lines are also useful for quantitative comparison of the effect of temperature on ductility for the two processing routes. The trend for Grade 304B5 is quite flat, as the average ductility of 304B5A is 1.51 times that of 304B5B at room temperature, and this ratio increases slightly to 1.53 at 400°C (752°F). For the 304B7 Type material, the average ducility of 304B7A is 3.19 times that of 304B7B at room temperature, and this ratio decreases to 2.93 at 400°C (752°F). No plastic strain was observed in the 304B7B samples past the point of uniform strain, while samples of 304B7A always exhibited deformation (i.e., necking) past this point. This helps to explain why there is such a dramatic increase in ductility for 304B7A compared to 304B7B. For the case of Type 304B5 material, both Grades exhibited deformation and evidence of necking past the point of uniform strain, but the typical 304B5A sample exhibited 5-6% additional plastic strain past the point of uniform strain, while the typical 304B5B spercimen deformed only 1-2% past the uniform strain before fracture.

The PM-processed Grade A material also has a higher 0.2% offset yield strength as a function of temperature relative to the IM-processed Grade B material. This effect is shown in Figure 4, where the trend lines again represent cubic fits to data obtained by regression analysis. Within a given Grade of material, the higher boron content Type 304B7 material leads to increase yield strength levels at all temperatures relative to Type 304B5 material: this is consistent with previous data for both Grades of borated 304 stainless steel at room temperature and 350°C (662°F) (Martin 1988). The higher yield strength for the Grade A material is undoubtedly due, to some degree, to the finer dispersion of borides, but a decreased grain size could also contribute to the increase in yield strength. The yield strength of all four lots of material at 371°C (700°F) are consistently higher than the yield strength of 103 MPa typically observed for 304L stainless steel (Japser 1989). It should be pointed out that the increase in strength observed in the borated grades are not reflected in the ASTM A887 specification, which requires minimum yield and tensile strength values of 205 and 515 MPa, respectively, for all Types and Grades.

The same trends are observed if tensile strength, rather than yield strength, were used as the basis of strength comparison between the boron-containing Grades A and B and boron-free 304L. The higher tensile strength levels suggest that high-cycle fatigue properties of the borated grades could be slightly higher for the boron-containing material. Recent results for strain-controlled fatigue experiments conducted at SNL (Stephens and Hatch 1992) have indicated that 304B5A has lower fatigue properties than boron-free 300 series stainless steel (ASME 1969) at the high strain amplitude/low cycle end of the test matrix, but this degradation disappears at lower strain amplitudes, where the elastic strain amplitude is greater than the plastic strain amplitude. This data is shown in Figure 5. Further work is needed to extend these results to lower strain amplitudes and different boron-containing Types as defined in ASTM A887.

ASME CODE CASE INQUIRY - STATUS AS OF JULY, 1992

The tensile data for selected Types of Grade A material have been used to initiate an ASME Boiler and Pressure Vessel (B&PV) Code Case Inquiry (#N90-27) for borated stainless steel. The requested applications in this inquiry are for use in "the construction of component supports for storage or transport of new or spent-fuel assemblies." The initial inquiry covers 304B4A, 304B5A and 304B6A material, and is currently awaiting approval by Section III. 304B7A material is not included in this code case because its required minimum impact energy (14 Joules = 10 ft-lbs.) was not deemed adequate: a value of 21 Joules (15 ft-lbs.) is considered necessary for consideration in a code case. At present, this code case is written so as to exclude welded material from receiving structural credit in the design. If approved, this inquiry will result in the establishment of design stress intensity values by which the approved material can be used in



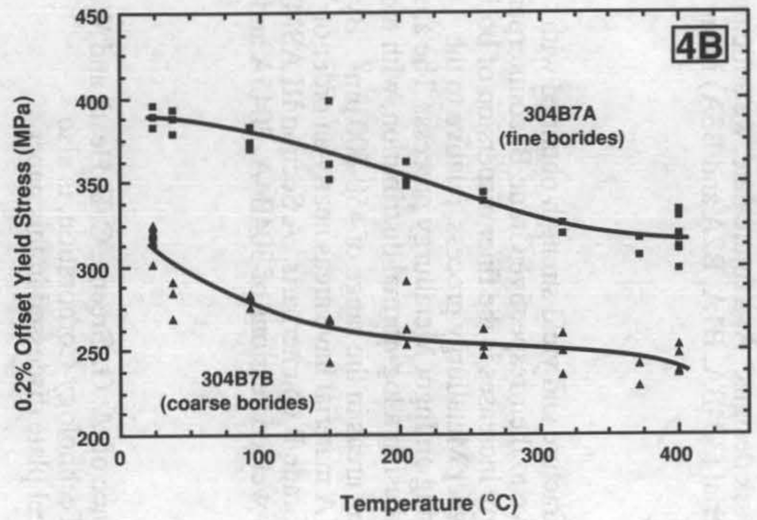


Figure 4. Yield strength (0.2% offset) as a function of temperature for all four lots of material studied in this paper. The trend lines drawn were obtained from regression analysis using a cubic equation. (a) 304B5A and 304B5B material. (b) 304B7A and 304B7B material.

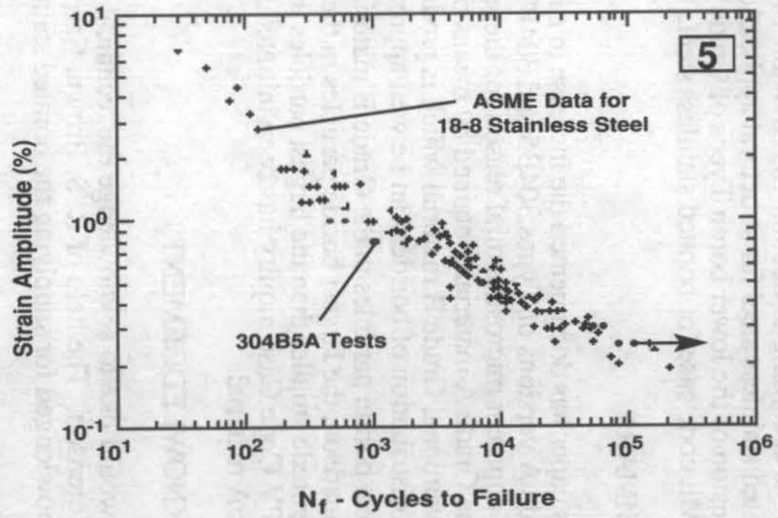


Figure 5. Room temperature, fully reversed low-cycle fatigue results for 304B5A are compared to the ASME data base for 300 series austentitic stainless steels. Strain-controlled tests run at a strain rate of $1x10^{-3}$ s^{-1} with a triangular waveform ramp using transverse samples.

designs according to Section III, Division 1 rules. This is an important step in qualifying borated stainless steel for structural applications in cask designs. At a future date, we anticipate inclusion of the lower boron Types of Grade A material (304BA, B1A, B2A and B3A) in an ASME code case for borated stainless steel.

SUMMARY

This paper has documented the increase in strain to fracture and yield strength obtained with Grade A versions of Types 304B5 and 304B7 relative to their respective Grade B, counterparts. The apparent microstructural reason for these property increases is the finer dispersion of boride in the Grade A material, obtained by means of a Powder Metallurgy process, relative to the conventional Grade B material which is produced using an Ingot Metallurgy process. The area size distribution of borides can be well approximated using a log-normal distribution, with the largest boride particles in the Grade B material having areas in the range of 450-600 μm^2. By comparison, the largest boride particles in the Grade A material have areas nearly an order of magnitude smaller than the largest particles in their Grade B counterparts. A Section III ASME B&PV Code Case inquiry has been initiated for non-welded versions of 304B4A, 3045A and 3046A material.

ACKNOWLEDGEMENTS

We would like to acknowledge the technical assistance of A. G. Greene, C. E. Heath and W. R. Sorenson. The help of R. S. Brown, Carpenter Technology Corporation, is also acknowledged for supplying the borated stainless steel plate discussed in this paper.

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