Factors affecting impact toughness in stabilized intermediate purity 21Cr ferritic stainless steels and their simulated heat-affected zones

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ABSTRACT

The correlation between simulated weld heat-affected zone microstructures and toughness parameters has been investigated in four intermediate purity 21Cr ferritic stainless steels stabilized with titanium and niobium either separately or in combination. Extensive Charpy-V impact toughness testing was carried out followed by metallography including particle analysis using electron microscopy. The results confirmed that the grain size and the number density of particle clusters rich in titanium nitride and carbide with an equivalent circle diameter of 2 μm or more are statistically the most critical factors influencing the ductile-to-brittle transition temperature. Other inclusions and particle clusters, as well as grain boundary precipitates are shown to be relatively harmless. Stabilization with niobium avoids large titanium-rich inclusions and also suppresses excessive grain growth in the heat-affected zone when reasonable heat inputs are used. Thus, in order to maximize the limited heat-affected zone impact toughness of 21Cr ferritic stainless steels containing 380–450 mass ppm of interstitials, the stabilization should be either titanium-free or the levels of titanium and nitrogen should be moderated.

1. INTRODUCTION

Lately several stainless steel producers have introduced and standardized 20–24 pct by mass Cr ferritic stainless steel grades [1–5]. These cost-efficient high-Cr steels have similar corrosion resistance to the common AISI 304 and 316 austenitic stainless steels, and are not to be mixed with the 26–29Cr + Mo superferritic steels of the 1970s that have been used in more demanding corrosive environments. Typically these recently developed high-Cr ferritic grades have low Ni and Mo contents to ensure stable and predictable alloying costs as well as stabilizing elements Ti, Nb, etc. that trap interstitial C and N so that sensitization to intergranular corrosion is suppressed.

Unlike austenitic steels, ferritic steels undergo a ductile to brittle transition in their fracture behavior. Therefore, replacement of austenitic grades with ferritic grades requires care to be taken in design to ensure that sufficient resistance to brittle fracture is maintained in the structures even after welding [6]. The total content of interstitial C and N is generally agreed to be the most critical factor for determining the toughness of fully ferritic stainless steels that do not undergo phase transformation to austenite and/or to martensite [7–12]. Low solubility of interstitials in ferrite leads to rapid, virtually inevitable, precipitation of carbonitrides at low temperatures. Ultimately, these brittle particles solely, in clusters, or in particle networks such as in grain boundaries may induce microcracks that then in turn provide nucleation sites for cleavage cracks [13–17].

Intermediate purity steels with interstitial levels of 250 to 500 mass ppm are typically obtained when the steels are produced using argon-oxygen decarburization (AOD). Ultra-pure interstitial levels of about 100 ppm and below are needed if superior toughness is desired, but costly vacuum steelmaking techniques have to be used to achieve these levels [7,9,18,19]. In intermediate purity stabilized steels, comparatively large inclusion and precipitate clusters can exist in the ferritic matrix. During casting, stable oxide inclusions such as Al_2O_3 and TiO_2 provide substrates for $\text{Ti}(\text{C},\text{N})$ nucleation and growth from the molten state. Typical hot working and annealing temperatures in the range 1073–1523 K (800–1250 °C) allow further coarsening of the carbonitrides and large conglomerations of particles are seen after cold working and annealing. In the weld heat-affected zone (HAZ) of ferritic stainless steels, some of the precipitates dissolve and re-precipitate intergranularly and intragranularly [20]. This process is usually termed as high-temperature embrittlement (HTE) that reduces toughness and corrosion resistance although stabilized grades are less susceptible to the phenomenon [21]. The location and magnitude of precipitation depends upon chemistry but also on cooling rate, slow cooling promoting intergranular precipitation.

Although plentiful research has been carried out to understand factors affecting to toughness in ferritic stainless steels, research into the overall effects of particle size, distribution and type together with grain size has been lacking. Moreover, the literature dealing with the toughness of stabilized intermediate purity 20–24 Cr ferritic stainless steels is limited due to their relative recent development, and research related to the effects of welding on the toughness of these steels is practically nonexistent. In this study, we provide analyses of the critical factors influencing the impact toughness of these steels and explain how the already limited HAZ toughness can be maximized through alloy and welding parameter design.

II. EXPERIMENTAL

A. Materials

Four intermediate purity stabilized ferritic stainless steels A–D were laboratory cast in a vacuum induction furnace as 65 kg ingots, the compositions are shown in Table I. The stabilization of the materials varied from fully Nb-stabilized (A), through dual-stabilized (B, C) to fully Ti-stabilized (D). All of the steels satisfied the standard stabilization formula $\text{Ti}+\text{Nb} \geq 0.2+4(\text{C}+\text{N})$, i.e. the alloys were over-stabilized with respect to C and N.

The 48 mm thick slabs were soaked at 1388 K (1115 °C) for 75 minutes and hot rolled to a thickness of 5 mm using approximately 30 pct reduction per pass finishing around 1053 K (780 °C). The materials were then cold rolled to a thickness of 3 mm and finally annealed in the range 1198–1303 K (925–1030 °C) for 1 minute followed by air cooling to achieve full recrystallization with a grain size of 20–30 μm .

B. Methods

Thermo-Calc software version 5.0.0.6053 (Thermo-Calc Software AB, Stockholm, Sweden) with a database TCFE7 was used to calculate the equilibrium phase balances and the chemistry of particles for the experimental steels in the temperature range 773–1973 K (500–1700 °C) using the elements Fe, C, Mn, Cr, Cu, N, Nb and Ti.

A Gleeble 3800 thermomechanical simulator (Dynamic Systems Inc., Poestenkill, NY) was used to simulate HAZs for three widely different heat input scenarios; 0.3, 0.5 and 0.9 kJ/mm, which translate into $\Delta t_{8/5}$ cooling times of 23, 65 and 210 seconds, respectively. Due to the 3 mm sample thickness a Rykalin 2D heat flow equation was used together with the following values: heating rate 300 degrees/s, peak temperature 1623 K (1350 °C), holding time at peak 0.1 s, free span 20 mm, density 7.7 g/cm³, specific heat 460 J/kgK, and thermal conductivity 26 W/mK. The heating rate was obtained from thermocouple measurements of prior gas tungsten arc welding tests on the same materials.

Sub-sized Charpy-V notched samples of 3 x 10 x 55 mm in the L-T orientation were used to minimize the effects of longitudinal strings of inclusions, which could act as crack paths for T-L orientated specimens. The

L-T orientation means the long side of the Charpy specimen is parallel to the longitudinal, i.e. rolling direction, and the V notch is made in the side perpendicular to the transverse direction. For the T-L orientation, the opposite is true. The criterion for the ductile-to-brittle transition temperature (DBTT) was set to 35 J/cm², i.e. 8.4 J for the 3 mm sample thickness. Typically, three samples were tested at each temperature and DBTTs were determined from *tanh* fitted transition curves as described by Wallin [22]. The amount of ductile fracture was determined from the fracture surfaces visually that was then used to determine the upper shelf energy (USE) for the variants. If no samples with 100% ductility existed, Wallin's upper-shelf energy estimation formula (1) was used with an exponent *m* value of 0.3 based on previous investigations [23]. Lower-shelf energy was fixed to 9 J/cm².

$$\frac{C_v}{C_{v-us}} \approx \frac{1+m}{2} \cdot \left[\left(\frac{SA}{100\%} \right)^m + \frac{1+m}{1-m} \left(\frac{SA}{100\%} \right)^{1+m} \right] \cdot 100\% \quad (1)$$

where C_{v-us} is the upper shelf energy of a sample, C_v is the impact energy of a sample, *m* is a constant, and *SA* is the amount of ductile fracture in a fracture surface as judged by eye.

Metallographic samples were prepared using water grinding and polishing with a diamond suspension to 1 µm. Microstructures of the samples were optically examined using Vilella's reagent and grain sizes were determined using the mean linear intercept method. Furthermore, samples used for scanning electron microscopy (SEM) were chemically polished with a 0.05 µm colloidal silica suspension. Vickers hardness (HV1) was measured with LECO M-400-H1.

Precipitate and inclusion structures were characterized using combined energy-dispersive X-ray spectrometry (EDS) and SEM. About 8000 particles were analyzed in total by using the *feature detection* routine of INCA software (Oxford Instruments, Abingdon, UK). The analysis for each sample was made using a total area of 8.4 mm² based on 30 randomly selected frames of 0.0276 mm². Only particles with an equivalent circle diameter (ECD) greater or equal to 1.0 µm were analyzed. The SEM-EDS analyses of the particles were normalized by assuming that any Fe signal came entirely from the steel matrix. The upper limit for the matrix contribution was set to 70 pct by mass, after which the results were considered to be too inaccurate for analysis. After the removal of the matrix contribution and the normalization process, the analyzed particles were grouped into various oxide and carbonitride compound systems based on their dominant elements. The individual elements in a stoichiometric compound were subtracted until one of the components was depleted, and then any remaining portions of other elements were used to calculate the next compound. Partly following Gordon and van Bennekom [24], these calculations were made in the order: Al₂O₃, TiO₂, TiN, NbN, TiC, NbC and Cr₂₃C₆, i.e. based on the approximation that, with falling temperature, these simple compounds form sequentially in the order given and ignoring any mutual solubilities. After all calculations, the mass pct of the elements in a particle were converted into volume pct by using known densities of the compounds. Finally, for further analysis, particles were classed according to their dominant simple compound, i.e. the compound which comprised more than half of the volume of the particle, e.g. Al₂O₃, TiO₂ etc. Those particles that did not have a dominant compound were classed as multiple oxide-carbide-nitrides. The entire process is schematically presented in Fig. 1.

Fig. 1 – Schematic process for SEM-EDS particle analysis

In addition, the smallest inclusions and precipitates in steel C were also examined by using electrolytic extraction as described in detail in Ref. [25]. Briefly, this technique uses multistep extraction and filtration based on dissolution of the matrix in an HCl electrolyte. Samples from the base metals and HAZs with a mass of about 2 g resulted in about 0.2 g of material being electrolytically extracted. After the electrolytic extraction, a polycarbonate film with a pore size of 0.1 μm was used for filtration. After the filtration, a piece of a film filter was cut, placed on an adhesive carbon tab and coated with carbon. Then, particles were examined with SEM-EDS using the feature detection routine. In order to analyze the smallest particles using a JEOL (Japan Electron Optics Laboratory Co., Ltd., Akishima, Tokyo, Japan) JEM-2200FS scanning transmission electron microscope (STEM) equipped with EDS, another piece of film filter was cut, submerged into methanol and exposed to ultrasound. Then, drops of methanol-particle dispersion were applied to carbon coated copper STEM sample grids.

Multiple linear regression model was built to explain factors influencing to DBTT by combining the chemical composition, grain size, hardness and particle details into one database in Minitab 17 software (Minitab Inc., PA, US). In the first stage, dozens of variable combinations were evaluated with less-restrictive α -level of 0.1–0.25 to identify the variables that might be associated with DBTT. In the second stage, best combinations were assessed with an α -level of 0.05 in simultaneous and hierarchical order. Variance inflation factor (VIF) was used to assess the multicollinearity of the independent variables. Collinear variables ($\text{VIF} > 5$) were treated so that the variable with strongest relationship was included in the final model.

III. RESULTS

A. Microstructures

Figures 2–5 show the optical micrographs of the unaffected base metals and simulated HAZs on cross-sections containing the rolling and thickness directions. The largest variations in the microstructure were seen with the unaffected base metals. In the fully Nb-stabilized steel A, the base metal microstructure contained large Nb carbonitride clusters but also smaller intragranular and intergranular particles (Fig. 2a). As the stabilization became more Ti-rich in steels B, C and ultimately D, the microstructures became increasingly ‘cleaner’, i.e. small precipitates were relatively scarce and large Ti/Nb carbonitride clusters occupied otherwise clean ferrite grains (Fig. 4a and Fig. 5a). Equilibrium phase diagrams calculated using Thermo-Calc predicted that in fully Ti-stabilized steel D the Ti(C,N) precipitation can begin in the molten state at 1804 K (1531 °C), which is 35 degrees above the predicted ferrite liquidus temperature, i.e. 1769 K (1496 °C). In steel C, the Ti(C,N) precipitation could initiate 5 degrees prior the solidification of ferrite 1772 K (1499 °C) and the solvus of Nb-rich (Nb,Ti)C precipitates is predicted to be in the solid state at 1363 K (1090 °C). Conversely in steel B, the Ti(C,N) is expected to precipitate during the solidification of ferrite, i.e. below 1768 K (1495 °C) and Nb-rich (Nb,Ti)C to precipitate in the solid state below the solvus at 1479 K (1206 °C). And finally in steel A, the Nb(C,N) precipitation was predicted to begin entirely from the solid state 1603 K (1330 °C). The above predictions are, however, based on equilibrium phase diagrams: the effects of interdendritic segregation and diffusion kinetics are ignored.

After HAZ simulations the microstructural differences became less distinct. The majority of large particle clusters vanished and were replaced with fine intragranular dispersion *clouds* of precipitates and intergranular grain boundary precipitates. The dissolution process was very apparent in steels B, C and D as all the precipitates that surrounded the yellow cuboidal titanium nitrides (presumably mostly carbides) were dispersed into the vicinity of the practically unaffected nitrides. These dispersion clouds were the most distinct with the low heat input scenario (Fig. 3b, Fig. 4b and Fig. 5b). As the heat input increased, i.e. the cooling rate decreased, the microstructures became more similar to each other in all steels (Fig. 3c–d, Fig. 4c–d and Fig. 5c–d). The only obvious exception was the absence of cuboidal nitrides in steel A (Fig. 2b–d).

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Fig. 2 - Optical microstructure of Nb-stabilized steel A after heat input simulations. Unaffected base metal (a), low 0.3kJ/mm (b), medium 0.5 kJ/mm (c), and high 0.9 kJ/mm heat input (d).

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Fig. 3 - Optical microstructure of dual-stabilized steel B after heat input simulations. Unaffected base metal (a), low 0.3kJ/mm (b), medium 0.5 kJ/mm (c), and high 0.9 kJ/mm heat input (d).

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Fig. 4 - Optical microstructure of dual-stabilized steel C after heat input simulations. Unaffected base metal (a), low 0.3kJ/mm (b), medium 0.5 kJ/mm (c), and high 0.9 kJ/mm heat input (d).

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Fig. 5 - Optical microstructure of Ti-stabilized steel D after heat input simulations. Unaffected base metal (a), low 0.3kJ/mm (b), medium 0.5 kJ/mm (c), and high 0.9 kJ/mm heat input (d).

206 *B. Particle analyses*

207 Basic characterization data of the materials after annealing and thermal simulation tests are shown in Table
208 II. A gradual increase in the grain size is seen as the welding heat input increased. With the highest heat
209 input scenario the mean grain size in the HAZ increased to 6–10 times that of the unaffected base metal, i.e.
210 from 19–31 µm to 180–210 µm. Surprisingly, the average (detectable) particle size remained relatively
211 unchanged regardless of the heat input used. The Nb-stabilized steel A had the finest average particle size
212 and only in a few cases $\varnothing \geq 3$ µm particles were observed. Interestingly, the particle count for $\varnothing 1$ –1.9 µm
213 particles in steel A noticeably increased from low heat input 8.2 pcs/frame to high heat input 34.2 pcs/frame.
214 This perhaps indicated that the smallest precipitates in the 0.30 and 0.50 kJ/mm heat input scenarios were too
215 small to detect with SEM-EDS feature run.
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The particles were further divided into compound system groups based on their chemistry and these are listed in Table III. It must be emphasized that these groups are merely estimates concerning the dominant compound in the particles. For instance, Fig. 6 demonstrates how at equilibrium the C and N concentrations can vary in carbonitrides with respect to temperature in steels A and D, i.e. close to the molten state the amount of N in a particle is the highest and C the lowest.

As was already shown from the micrographs, the absence of TiN-rich particles in steel A can also be seen from the Table III. Noticeable differences between the materials were also the presence of TiC-rich particles in steel D and NbC-rich particles in steel A. Although all steels were deoxidized with Al the EDS spectrum from the nitrides likely obscured the spectrum from the oxide core in steels B–D unlike in steel A where the small Al_2O_3 particles were evident.

Fig. 6 – Change of C and N concentrations with respect to temperature in Nb(C,N) of steel A (a) and Ti(C,N) of steel D (b) at equilibrium. Calculated via Thermo-Calc.

Due to somewhat large separation of the dispersion clouds from the yellow cuboidal nitrides after HAZ simulations (e.g. Fig. 4b), additional analyses were carried out for particles $\varnothing < 1 \mu\text{m}$ in steel C using the electrolytic extraction method. Because carbon coating was used, the SEM-EDS data in Table IV lists only substitutional elements. As can be seen, the particles were mostly Ti and Nb-based with the occasional presence of Cr and only minor amounts of other elements. In Fig. 7 a series of micrographs show the smallest spherical, cuboidal and needle-like particles detected via STEM. Albeit only few particles were quantified with STEM-EDS, a similar tendency could be seen that the smallest particles were based on Ti and Nb, Fig. 8.

Fig. 7 - STEM images of extracted particles in low 0.3 kJ/mm heat input scenario of dual-stabilized steel C.

Fig. 8 - STEM-EDS analyses of extracted particles in low 0.3 kJ/mm heat input scenario of dual-stabilized steel C: 54%Nb, 29%Ti, 11%Cu, others (Cr, Fe) <5 % (a) and 52%Nb, 20%Cr, 17%Ti, others (Cu, Fe) <5% (b).

C. Impact toughness

The data from the impact toughness tests is summarized in Table II and the fitted transition curves are shown in Fig. 9. All in all, the DBTT (35 J/cm²) range was 80 degrees, including the base metals and simulated HAZ. The table also lists the USE values, and on average, the estimated values were on par with the experimentally determined values (160 ± 11 J/cm² vs. 159 ± 14 J/cm², respectively). In the base metals, the Nb-stabilized steel A showed the lowest and Ti-stabilized steel D the highest DBTT. Generally, an increase in the DBTT was seen with the examined steels as the welding heat input increased. Also, the transition curves became less steep with the higher heat inputs.

Fig. 9 - Charpy-V *tanh* fitted transition curves of all steels and heat input simulations.

D. Fractography

Fractured Charpy samples in the transition range showed that fracture micromechanisms were as expected. Ductile parts failed by microvoid coalescence and brittle parts by multifaceted transgranular cleavage as demonstrated in Fig. 10. The amount of ductile fracture in the fractured surface was generally no more than 10% at the 35 J/cm² transition temperature. The intensive grain boundary precipitation in the simulated HAZ samples did not lead to intergranular fracture. Microvoids frequently contained inclusions and precipitates and large nitrides were easily distinguishable from the cleavage planes. Despite extensive search for cleavage crack nucleation sites near the notch of Charpy samples, only few particles could be identified to potentially act as nuclei, Fig. 11.

Fig. 10 - Mixed microvoid and cleavage fracture (a) and multifaceted cleavage fracture (b) observed in Ti-stabilized steel D.

Fig. 11 - Potential fracture initiation sites in steel D: grain boundary TiN (a), intragranular TiN (b), intragranular Ti-rich particle (c). Initiation site with no detectable particle in steel A (d).

E. Statistical analyses

Several DBTT models were built by combining the chemical composition (Table I), grain size and particle details (Table II), and more specific particle groups and size classes (Table III). In all preliminary models, the effect of grain size was very significant and had a large effect on the DBTT: it alone explained more than a half of the variance in the data ($\text{adj. } R^2 = 0.55$). Hardness appeared to have no significant effect on the DBTT; however, hardness values only vary over the range 152–168 HV1. Grain size with mean particle diameter explained two-thirds of the variance in the data ($\text{adj. } R^2 = 0.67$). Grain size with particle count ($\text{ECD} \geq 2\mu\text{m}$) further improved the correlation ($\text{adj. } R^2 = 0.70$). More specific analysis based on Table III indicated that grain size together with TiN-rich and TiC-rich particle groups explained 77% of the variance in the DBTT. Ultimately, the best regression model ($\text{adj. } R^2 = 0.80$, $\text{SE} = 10$ degrees) presented in Table V and Fig. 12 shows that grain size was the most contributing factor to DBTT followed by the total number density of large TiN-rich and TiC-rich particles ($\text{ECD} \geq 2\mu\text{m}$).

Fig. 12 - Predicted vs measured DBTT.

IV. DISCUSSION

The results of this study suggest that there are two main factors influencing impact toughness in stabilized intermediate purity 21Cr ferritic stainless steels and their HAZs. A strong statistical significance was seen that the grain size and large, i.e. $\varnothing \geq 2\mu\text{m}$ Ti-rich carbonitride particles increase the DBTT considerably. For example, the influence of TiN-rich particles on brittle fracture in our study could be demonstrated with steels B, C and D: In the highest heat input scenario (0.9 kJ/mm) the microstructures were very similar regardless of the Ti/Nb stabilization ratio, the grain sizes were large ($\geq 180\mu\text{m}$) and the amount of large TiN-rich particles was high. Consequently, the toughness was about equal ($\text{DBTT} = 43\text{--}48^\circ\text{C}$).

Overall, the results agree well with the general literature on ferritic stainless steels. Nb stabilization in the base metal should result in improved toughness over Ti stabilization [14,26]. Han et al. [14] showed that for 18Cr-2Mo steels large TiN particles would usually initiate cleavage cracks and reduce the toughness compared to solely Nb+V -stabilized steel. Grubb et al. [13] demonstrated that in high-purity Fe-26Cr steels Ti alloying promotes intergranular microcracks and reduced toughness even when the precipitation has been limited by fast cooling. Li et al. [15] also noticed similar effects in 18Cr-2Mo steels, but also suggested that fine Cr_2N had a role in decreasing the toughness. In our case the smallest detected precipitates were predominantly Ti and Nb-based so that the presence and effect of Cr_2N is probably small. In other ferritic steels, Ghosh et al. [16] described how relatively small $> 0.5\mu\text{m}$ TiN could initiate cleavage cracks in high strength low alloy (HSLA) steels. However, Du et al. [17] found no statistical significance between DBTT and TiN particles in such steels.

The formation of microcracks in brittle particles has been proposed to initiate cleavage cracks [13–17]. Ghosh et al. [16] described that Al_2O_3 that are frequently found at the core of TiN in Al-killed steels could already promote enough internal microcracking that would at low stress propagate to particle-matrix interface. When the crack length is assumed to be similar in size to the particle diameter, a steep decrease in the local fracture stress occurs as the particle size increases. Consequently, the crack propagates from the

particle to the ferrite grain. Then, a critical grain size exists that determines whether or not the grain boundary is able to arrest the cleavage crack from penetrating through multiple high-angle grain boundaries [16].

Typically in the literature of ferritic stainless steels, grain boundary precipitation promoted by slow cooling is considered to be detrimental to toughness in ultra and intermediate purity unstabilized steels [6,27]. In our case this effect was either small or hindered by the stabilization. For example, in steel D the toughness was not significantly reduced with low and medium heat inputs compared to the unaffected base metal despite the increase in grain size and grain boundary precipitation that surrounded basically every grain. In the intermediate purity stabilized ferritic steels alloying with Ti has been shown to lower the DBTT when compared to unstabilized steels. Grubb [13] thought that the detrimental influence of Cr in intermediate purity steels comes from needle-like Cr precipitates. Once the Ti was alloyed, the DBTT was lowered due to reduced needle-like precipitation. In our study needle-like precipitates existed but had no significant effects on DBTT. However, the small precipitates were not considered in the regression analyses due to a lack of quantitative data. Also, they were not based on Cr but on Ti and Nb.

In contrast to the Ti-containing steels of this study, the DBTT of the HAZ in Nb-stabilized steel A remained practically unchanged regardless of the heat input used and resulting grain size (74 to 185 μm). Evidently, the absence of large particles made the crack initiation more difficult. However, based on hardness values, we consider that the HAZ in steel A had the highest strength in the low heat input scenario, presumably due to presence on fine Nb-rich particles. In medium and high heat input scenarios the hardening effect was not as severe. Thus, the decrease in the flow stress of the material and increase in grain size resulted in opposite effects on DBTT. Typically in ferritic stainless steels an increase of 1 ASTM number (decrease in grain size) should lower DBTT by 6–26 degrees but that higher interstitial content would reduce the improving effect due to precipitation [6,9,27,28]. In our study the influence of an increase in 1 ASTM grain size suppressed the DBTT 7–8 degrees, which meets these considerations.

The significant influence of large TiC-rich groups on DBTT was somewhat surprising. Ghosh et al. [16] pointed out that (grain boundary) carbides have higher surface energy than TiN so that microcracking of carbide requires 3–5 higher fracture stress, making carbides relatively weak sources for the initiation of cleavage cracks. In our case, we are cautious about the overall effect of TiC-rich particles because 1) only steel D contained sufficient amount of these and 2) quantitative analysis of carbon with SEM-EDS is known to be imprecise. We hypothesize that as the carbides in the base metal of steel D rarely were separated from cuboidal nitrides, e.g. the microstructure was distinctly ‘clean’, the apparent effect of TiC group was actually a combination of Ti particle clusters rather than solely Ti carbides. Moreover, as the equilibrium calculations indicated, the C and N levels in carbonitrides would always alter depending on temperature and chemistry.

The practical implications of this study are, that in the intermediate purity interstitial levels stabilization fully or partially with Ti runs the risk for the formation of large TiN/TiC-rich clusters that originate from the molten state. Thus, in order to maximize the limited impact toughness, either the stabilization should be Ti-free or the levels of Ti and N should be moderated to reduce the size of the particles forming from the interdendritic liquid. Stabilization with Nb also tends to suppress excessive grain growth in the base material and HAZ because of the combined effects of solute drag and Zener pinning. This was at least partially seen with steel A that showed the lowest grain size in the base metal, and in the HAZ for low and medium heat inputs. However, excessively high heat input, like the 0.9 kJ/mm used in this study for 3 mm sheet, led to extensive dissolution of precipitates and reduced the grain boundary pinning effect.

The main limitations of this study were the limited number of compound groups and the criteria used for grouping for the compounds in the particle analysis. As already stated, the particle analysis used in this paper assumes that the volumetrically largest compound in a particle will dominate the cleavage nucleation. Also, the size classes were determined by using ECD which does not take into account different particle morphologies. Therefore, for future studies it would be beneficial to take into account other particle systems such as sulfides, and the change in the composition of particles after HAZ simulations. Attention should also be paid to the relationship between impact toughness and fracture toughness. Redmond [26] demonstrated in 18Cr-2Mo welds that the stabilization methods may bring about different results in fracture toughness and

impact toughness testing. Also, recent work by Nevasmaa et al. [29] pointed out that the fracture toughness transition temperature (T_0) and impact toughness transition temperature (T_{28J}) correlation may not be suitable for the stabilized ferritic stainless steels.

V. CONCLUSIONS

Our study suggests that grain size and Ti carbonitride particles with an equivalent circle diameter greater than 2 μm govern the impact toughness of the base metal and HAZ in 21% Cr intermediate purity ferritic stainless steels. The research also verified the generally found fact that Nb stabilization results in better performance over dual-stabilization or Ti stabilization in the base metals and simulated HAZ of ferritic stainless steels. Large Ti carbonitride clusters that originate from the molten state can grow further through solid state precipitation. TiN-rich particles are practically unaffected by the welding heat input and act as nuclei for cleavage cracks. Conversely, Nb stabilization generally promotes smaller solid state precipitates and the absence of large particles makes the Nb-stabilized steel relatively tolerant to variations in heat input. It must be emphasized that we only used 8 particle groups, assumed that volumetrically largest particles dominate the cleavage nucleation, and that morphology had no effect. Further research should also investigate how impact toughness correlates with fracture toughness with different methods of stabilization as fracture toughness is more important than impact toughness from a design and dimensioning point of view.

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TABLES

Table I – Chemical compositions of the laboratory steels, mass pct

Steel	C	Si	Mn	S	P	Cr	Ni	Ti	Nb	Cu	Al	O	N	Fe
A	0.016	0.45	0.51	0.004	0.007	20.9	0.2	0.02	0.54	0.42	0.011	0.0041	0.022	Bal
B	0.021	0.47	0.31	0.003	0.006	20.9	0.2	0.11	0.34	0.42	0.010	0.0038	0.024	Bal
C	0.021	0.46	0.29	0.003	0.005	20.9	0.2	0.21	0.23	0.41	0.011	0.0048	0.023	Bal
D	0.029	0.45	0.29	0.003	0.006	20.2	0.2	0.53	0.01	0.42	0.023	0.0055	0.012	Bal

Analyses were made using ARL 4460 optical emission and ARL 9800 XP X-ray spectrometers, and LECO gas analyzer.

Table II – Basic characterization data for the examined steels.

Steel	Heat input kJ/mm	Grain size μm	Hardness HV1	DBTT $^{\circ}\text{C}$	USE J/cm ²	Mean particle size* μm	No of particles per frame divided into size classes*		
							1–1.9 μm	2–2.9 μm	$\geq 3 \mu\text{m}$
A	Base	19 $\pm$ 3	154 $\pm$ 3	-35	155	1.3 $\pm$ 0.3	55.2	2.5	0.2
	0.30	74 $\pm$ 11	168 $\pm$ 3	4	150 ^x	1.3 $\pm$ 0.2	8.2	0.2	0.0
	0.50	106 $\pm$ 28	164 $\pm$ 2	-2	154 ^x	1.4 $\pm$ 0.3	7.9	0.5	0.0
	0.90	185 $\pm$ 21	159 $\pm$ 5	4	149 ^x	1.4 $\pm$ 0.4	34.2	2.3	0.4
B	Base	30 $\pm$ 7	152 $\pm$ 2	-17	177	2.1 $\pm$ 0.9	4.0	1.8	1.3
	0.30	94 $\pm$ 14	161 $\pm$ 3	-8	160 ^x	2.2 $\pm$ 1.0	6.8	3.5	2.2
	0.50	119 $\pm$ 28	155 $\pm$ 2	18	172 ^x	2.2 $\pm$ 0.9	5.4	3.5	2.2
	0.90	210 $\pm$ 39	155 $\pm$ 3	37	185 ^x	2.2 $\pm$ 0.9	5.0	3.2	2.0
C	Base	28 $\pm$ 4	153 $\pm$ 3	-5	167 ^x	1.9 $\pm$ 0.7	6.2	3.3	0.8
	0.30	95 $\pm$ 13	157 $\pm$ 5	14	157 ^x	2.0 $\pm$ 0.7	8.4	5.2	1.6
	0.50	124 $\pm$ 19	160 $\pm$ 3	28	166 ^x	2.0 $\pm$ 0.7	10.6	5.5	1.4
	0.90	180 $\pm$ 20	155 $\pm$ 5	52	171	2.2 $\pm$ 0.8	5.8	4.9	2.1
D	Base	31 $\pm$ 7	158 $\pm$ 4	12	147	2.1 $\pm$ 0.8	9.3	7.1	2.2
	0.30	96 $\pm$ 12	159 $\pm$ 3	22	145	2.0 $\pm$ 0.7	7.9	5.4	1.0
	0.50	127 $\pm$ 21	162 $\pm$ 3	11	151 ^x	2.0 $\pm$ 0.8	9.1	6.5	1.9
	0.90	182 $\pm$ 12	158 $\pm$ 4	45	154 ^x	2.2 $\pm$ 0.8	7.0	5.6	2.3

Grain size = mean linear intercept $\pm 1\sigma$; frame = 0.0276 mm² = 27 600 μm^2 ; * estimated value using Eq. [1]; * size = equivalent circle diameter (ECD) in $\mu\text{m} \pm 1\sigma$

Table III – Compound groups calculated for analyzed particles

Steel	Heat input kJ/mm	No of particles per frame divided into compounds and their size classes (1–1.9 μm / 2–2.9 μm / $\geq 3 \mu\text{m}$)						
		Al ₂ O ₃	TiO ₂	TiN	NbN	TiC	NbC	Cr ₂₃ C ₆
A	Base	5.1 / 0.2 / -	4.2 / 0.1 / -	- / - / -	0.8 / - / -	- / - / -	41.7 / 2 / 0.2	0.9 / 0.1 / -
	0.30	1.8 / 0.1 / -	0.5 / - / -	- / - / -	- / - / -	- / - / -	5.8 / 0.1 / -	- / - / -
	0.50	2 / 0.1 / -	0.2 / - / -	- / - / -	0.1 / - / -	- / - / -	5.2 / 0.3 / -	- / - / -
	0.90	3.1 / 0.2 / 0.1	1.4 / - / -	- / - / -	0.4 / - / -	- / - / -	28.6 / 2 / 0.4	0.1 / - / -
B	Base	0.1 / 0.1 / -	0.1 / 0.1 / -	3.6 / 1.5 / 1.2	- / - / -	- / - / -	- / - / -	- / - / -
	0.30	0.1 / 0.1 / -	1.1 / 0.3 / 0.2	4.5 / 2.4 / 1.8	- / - / -	0.1 / - / -	0.4 / - / -	- / - / -
	0.50	- / 0.1 / 0.2	0.6 / 0.2 / 0.1	3.8 / 2.5 / 1.8	- / - / -	- / - / -	- / - / -	- / - / -
	0.90	- / 0.1 / -	0.2 / 0.2 / 0.1	4.2 / 2.7 / 1.9	- / - / -	0.1 / - / -	0.3 / - / -	- / - / -
C	Base	0.1 / 0.1 / -	- / 0.1 / -	6 / 3.1 / 0.7	- / - / -	- / - / -	- / - / -	- / - / -
	0.30	0.2 / 0.2 / 0.1	0.5 / 0.1 / 0.2	7.4 / 4.8 / 1.2	- / - / -	- / - / -	- / - / -	- / - / -
	0.50	1 / 0.6 / 0.2	0.8 / 0.4 / 0.1	7.8 / 4.2 / 1.1	- / - / -	0.1 / - / -	- / - / -	- / - / -
	0.90	- / - / 0.1	0.5 / 0.1 / -	4.9 / 4.6 / 1.9	- / - / -	- / - / -	- / - / -	- / - / -
D	Base	- / - / -	0.1 / - / -	0.2 / 1.4 / 0.9	- / - / -	8.8 / 5.2 / 0.7	- / - / -	- / - / -
	0.30	- / - / -	0.3 / - / -	1.5 / 3.2 / 0.8	- / - / -	5.2 / 0.8 / -	- / - / -	- / - / -
	0.50	0.5 / 0.6 / 0.1	0.2 / 0.1 / -	2.5 / 3.3 / 1.3	- / - / -	5.2 / 1.7 / 0.1	- / - / -	- / - / -
	0.90	- / - / -	0.1 / 0.1 / -	0.2 / 2.2 / 1.7	- / - / -	6.3 / 2.3 / 0.2	- / - / -	- / - / -

Table IV – Analyses of $\varnothing < 1 \mu\text{m}$ particles in steel C.

Location		Ti	Nb	Cr	Cu	S	Si
Base metal (n=1788)	Freq.%	95	92	29	48	46	12
	Mean, mass-%	43 $\pm$ 20	40 $\pm$ 23	3 $\pm$ 9	< 1 $\pm$ 1	7 $\pm$ 9	2 $\pm$ 10
HAZ 0.3 kJ/mm (n=4125)	Freq.%	95	95	52	15	–	–
	Mean, mass-%	31 $\pm$ 13	60 $\pm$ 16	5 $\pm$ 6	< 1 $\pm$ 4	–	–

Freq.% = frequency of an element being present in a particle with respect to the total number analyzed (n), < 10% not listed; Mean = normalized concentration of substitutional elements

Table V – Final multiple linear regression model to predict the DBTT

Variables	Coefficient	Cont.**	SE	95% CI	p-value	VIF
Intercept	-32.43					
Grain size	0.25	58%	0.04	0.16 to 0.35	< 0.001	1.03
TiN+TiC*	4.30	25%	1.00	2.14 to 6.45	0.001	1.03

* no of particles per 0.0276 mm² (ECD > 2 μm); ** contribution to variance

LIST OF FIGURE CAPTIONS

Fig. 1 – Schematic process for SEM-EDS particle analysis

Fig. 2 - Optical microstructure of Nb-stabilized steel A after heat input simulations. Unaffected base metal (a), low 0.3kJ/mm (b), medium 0.5 kJ/mm (c), and high 0.9 kJ/mm heat input (d).

Fig. 3 - Optical microstructure of dual-stabilized steel B after heat input simulations. Unaffected base metal (a), low 0.3kJ/mm (b), medium 0.5 kJ/mm (c), and high 0.9 kJ/mm heat input (d).

Fig. 4 - Optical microstructure of dual-stabilized steel C after heat input simulations. Unaffected base metal (a), low 0.3kJ/mm (b), medium 0.5 kJ/mm (c), and high 0.9 kJ/mm heat input (d).

Fig. 5 - Optical microstructure of Ti-stabilized steel D after heat input simulations. Unaffected base metal (a), low 0.3kJ/mm (b), medium 0.5 kJ/mm (c), and high 0.9 kJ/mm heat input (d).

Fig. 6 – Change of C and N concentrations with respect to temperature in Nb(C,N) of steel A (a) and Ti(C,N) of steel D (b) at equilibrium. Calculated via Thermo-Calc.

Fig. 7 - STEM images of extracted particles in low 0.3 kJ/mm heat input scenario of dual-stabilized steel C.

Fig. 8 - STEM-EDS analyses of extracted particles in low 0.3 kJ/mm heat input scenario of dual-stabilized steel C: 54%Nb, 29%Ti, 11%Cu, others (Cr, Fe) <5 % (a) and 52%Nb, 20%Cr, 17%Ti, others (Cu, Fe) <5% (b).

Fig. 9 - Charpy-V *tanh* fitted transition curves of all steels and heat input simulations.

Fig. 10 - Mixed microvoid and cleavage fracture (a) and multifaceted cleavage fracture (b) observed in Ti-stabilized steel D.

Fig. 11 - Potential fracture initiation sites in steel D: grain boundary TiN (a), intragranular TiN (b), intragranular Ti-rich particle (c). Initiation site with no detectable particle in steel A (d).

Fig. 12 - Predicted vs measured DBTT.

(a)

200 nm

Ti

100 nm

Ti K

Nb

100 nm

Nb L

Cr

100 nm

Cr K

(b)

200 nm

Ti

200 nm

Ti K

Nb

200 nm

Nb L

Cr

200 nm

Cr K