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SOLUBILITY AND PRECIPITATION OF Nb IN AN ANNEALED Fe-30Mn STEEL

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الملخص

التأثير الميتالورجي لعنصر النيوبيوم على سبائك الحديد عالي المنجنيز والملدن بالمعالجة الحرارية لا زال موضوع نقاش واهتمام بين شركات صناعة السيارات وشركات صناعة الحديد لاهمية هذا النوع من الصلب في صناعة هياكل السيارات. وموضوع هذا النقاش حسب المصادر العلمية ينصب حول تأثير ذوبانية النيوبيوم في الاستنيت على التركيب المجهري وبالتالي على الخواص الميكانيكية للسبيكة.

في هذا البحث يتركز الاهتمام على دراسة ذوبانية النيوبيوم على سبيكة الحديد المحتوية على 30% منجنيز حيث تمت اضافة النيوبيوم النقي بنسب مئوية تبدأ من 0.05 الى 1.0 على مسبوكات الصلب اثناء عمليات السباكة. والعينات المستعملة في الدراسة هي عينات منتجة بطريقة السباكة التقليدية (في الهواء الجوي) تمت معالجتها في درجة حرارة 1200 درجة مئوية وفي فترات زمنة، 2 و5 و 10 و 30 و60 دقيقة لغرض التلدين. وللكشف على البنية المجهرية والتعرف على تأثير عملية التلدين تم استعمال المجهر الالكتروني النافذ والمجهر الالكتروني الماسح المزود بوحدة التحليل الكيميائي لتحديد نوع المركبات المترسبة في محلول السبيكة الجامد بعد المعالجة الحرارية.

تم ايضا في هذه البحث الدراسة النظرية لذوبانية النيوبيوم اعتماداً على افتراضات العالم جلادمان كما تم اختبارها باستعمال برنامج تحليل ذوبانية العناصر (ثيرمو– كلك). لذا جاءت نتائج هذا البحث كمقارنة بين التجارب المعملية للبنية المجهرية والدراسة النظرية، ووُجِد ان عنصر النيوبيوم يذوب في سبيكة الأوستنيت مكونا عائق ساحب لحدود الحبيبات وان النسب العالية من هذا العنصر ايضا تكوَن المركبات المترسبة في طور الأوستنيت والتي لها تأثير يعيق نمو حبيبات الطور وكلا الحالتين تسببان في تحسين بعض الخواص الميكانيكية للسبيكة المحتوية على 30% منجنيز.

ABSTRACT

The metallurgical influence of niobium (Nb) on an annealed high manganese (Mn) steel is still an active issue of discussion between automobile companies and steel manufacturers. Some controversy exists in the literature concerning the influence of Nb solubility on microstructure and thereby on mechanical properties.

The influence of Nb-solubility on microstructure of Fe30Mn alloy steel was investigated experimentally and by computational materials modeling. Nb was added in 0.05, 0.1, 0.2, 0.4, 0.6 and 1% additions and the alloy samples were annealed at 1200ºC for 2, 5, 10, 30 and 60 minutes. The microstructure was investigated using an optical microscope, TEM and SEM-EDX and precipitates were chemically tested.

Niobium solubility in Fe30Mn austenite was theoretically studied based on Gladman assumptions and was also examined by Thermo-Calc analysis. The result of this work is a comparison between the microstructure analysis and theoretical studies, and it

has been found that Nb was soluble in Fe30Mn austenite phase and has had a solute drag effect where Nb(C,N) and NbN precipitates were seen and the effect was pinning effect.

KEYWORDS: Nb Solubility; High-Mn Steel; Solute-Drag Effect; Precipitate-Pinning; Thermo-Calc Analysis**.**

INTRODUCTION

The addition of alloying elements to establish microstructural control through thermo-mechanical processing of High Strength Low Alloy (HSLA) steels such as Twining Induced Plasticity (TWIP) steel, has been the most important endeavors of the past decade. This addition along with reducing the carbon content have made it possible to attain the desirable strength/ductility ratio for automobiles and other applications [1].

High manganese steel alloy with 30%Mn has a TWIP effect that occurs at room temperature but progressively transforms to dislocation glide when deformation temperature increases. Addition of Nb, Ti, V and/or Mo elements to TWIP steels, can have a significant influence on the kinetics of austenite recrystallization and grain growth. However, if these elements are not precipitated, they remain in the austenite matrix providing a solute drag effect that delay recrystallization and suppresses grain growth. The degree to which austenite grain growth is inhibited will depend on the size and the volume fraction of the precipitates as well as the level of solute elements [2, 3]. S. Koyama et.al [4], have studied theoretically the solubility of Nb in high-Mn steels with different Mn contents (but up to 10%Mn), and they found that Mn increases the solubility of NbC and decreases the solubility of NbN but as temperature increases this effect becomes weaker.

The present research involves the study of the Nb solubility in an annealed high Mn steel to understand at what Nb level pinning or solute drag effect can occur. This includes study of solubility products using Thermo-Calc software and empirical equations, as well as analysis of precipitates, and microstructure study. Conventional casting of Fe30Mn alloy and different annealing temperatures both employed to produce experimental materials.

EXPERIMENTAL WORK

The alloy used in this study is Fe30Mn (TWIP) steel. This high-Mn alloy has a stable austenitic structure and no martensite is expected [5, 6]. The steel alloy used in this study was a conventional casting Fe30Mn (produced at Deakin University Laboratories). In conventional casting line, ferrous iron (containing 0.037% carbon/1 kg) and Ferromanganese (containing 0.003% carbon/1 kg) was added to the molten solution at approximately 1500ºC. Ferro-niobium Fe-Nb (containing 0.08% carbon/1 kg), was added to the 30Wt% Mn-steel solution at approximately 1500ºC and samples were taken to the metal analyzer (Spector MAXx) and the result is given in Table (1). Due to conventional casting and challenging to control the carbon content, the studied samples will be divided in to low Nb group with very low carbon content that can be neglected (<0.008%), and high Nb group alloys with low carbon content (0.01 to 0.012%).

Samples of 20x15x2.5 mm were taken to a fluid bed furnace (Furnace-FH24H) for annealing to 1200ºC for times of 2, 5, 10, 30 and 60 minutes followed by air cooling.

For all, SEM, TEM and SEM-EDX investigations, the samples were ground using 240, 600 and 1200 grit silicon carbide grinding papers. Next, each sample was polished using 9, 3 and 1-micron diamond pastes on a rotary plate. Etching process using saturated aqueous 7% solution of sodium Meta bi-sulphate was used at room temperature for approximately 2 minutes to etch the prior austenite grain boundaries and deformation structure. Some samples were chosen for TEM analysis, they were electro-polished using a twin jet electro-polisher and a solution of 5 vol.% perchloric acid, 20 vol. % glycerol and 75 vol.% industrial methanol. The electro-polishing was performed with the solution at 0ºC, the electrical potential being set at 50V for all specimens. Microstructure observations and microphotography were carried out using (OLYMPUS BX51M) optical microscope and the annealed Nb-TWIP specimens were examined using thin foil techniques in TEM (JEOL 2100F).

Table 1: Chemical composition of studied TWIP alloys

Sample No.	Chemical Composition (wt.%)			
	Mn	Nb	C	N
0.0	29.2	0.0001	0.002	0.0026
0.05	29.7	0.044	0.002	0.005
0.1	29.9	0.078	0.004	0.007
0.2	30.02	0.18	0.008	0.01
0.4	30.1	0.46	0.008	0.011
0.6	30.2	0.62	0.013	0.011
1.0	30.4	1.0	0.021	0.012

Imaging was carried out for different samples in different cases of heat treatment and precipitation particles were observed with different morphologies. Precipitated particle size measurement was performed on SEM images using Image software. A semi-qualitative analysis of precipitates was made for most precipitates through the use of Energy-Dispersive X-ray (EDX) techniques using a SUPRA-55VP (SEM).

RESULTS AND EXPERIMENTAL OBSERVATIONS

Microstructural investigations of the Nb-added Fe30Mn samples show a different rate of grain growth of the two alloy groups. It is observed that the grain sizes of the lower Nb alloys are always the largest, while those in alloy 0.6Nb and 1Nb are the finest. It also shows full recrystallization occurred at short annealing times for the low-Nb (0.05, 0.1, and 0.2%) alloys. But for high-Nb alloys, high recrystallization fractions were seen in the 1200ºC/5 minutes annealed structure and was fully recrystallized when those samples were held for 30 minutes as shown in Figure (1) (samples from 0.4Nb and 0.6Nb alloys as an example).

Electron microscopy studies using angle selective backscattering detector (AsB) under different kv were carried out for a selected number of annealed Nb-added samples in order to investigate the possible presence of coarse undissolved Nb precipitates in the annealed 1200ºC samples. As shown in Figure (2), coarse precipitated particles were seen in 0.6Nb samples whereas no particles were able to be seen in low-Nb samples.

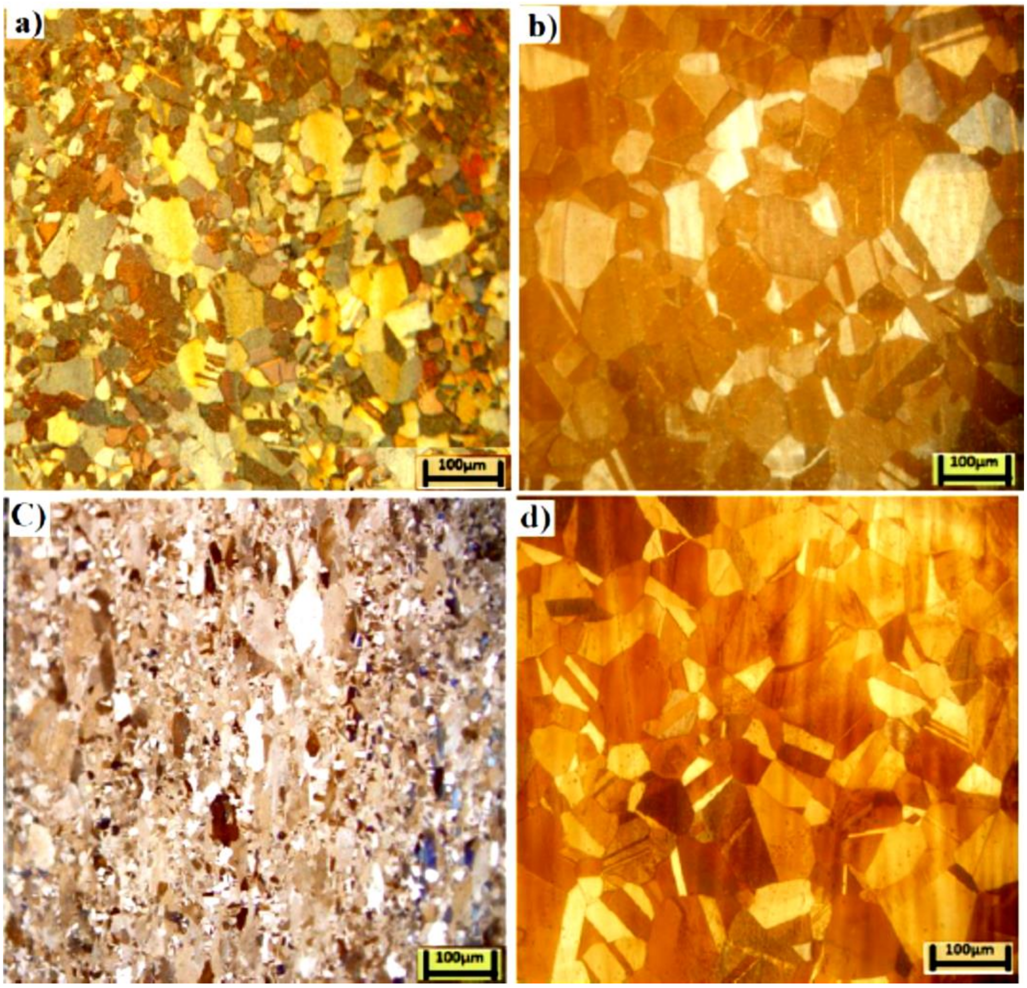

Figure 1: Optical micrographs showing grain growth of annealed Nb-added Fe30Mn samples a) 0.4 sample at 1200ºC/5, b) 0.4 sample at 1200ºC/30, c) 0.6 sample at 1200ºC/5, and d) 0.6 sample at 1200ºC/30 minutes.

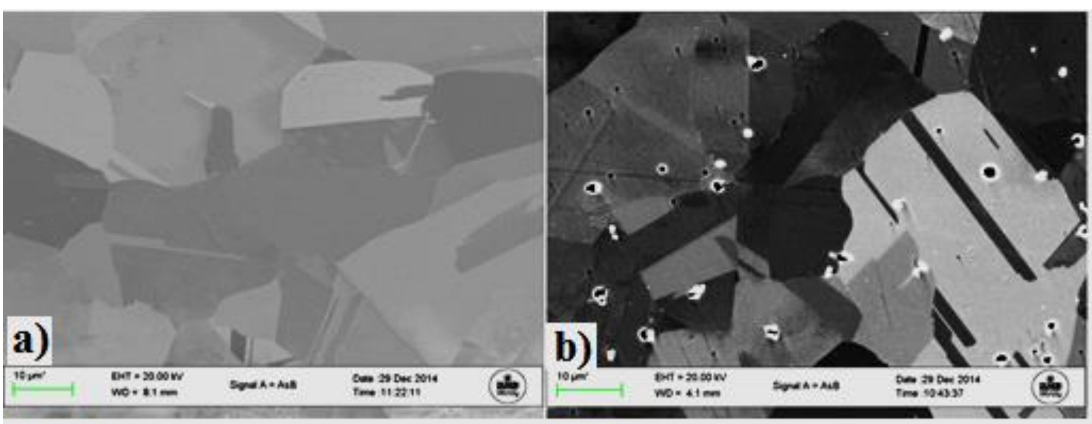

Figure 2: SEM-AsB images of annealed 1200ºC/30 minutes for; a) no precipitation seen in samples of 0.4Nb, and b) the presence of coarse precipitates (white particles) in 0.6Nb sample.

TEM analysis identified the presence of coarse and intermediate particles in the annealed microstructure of the high Nb alloys as shown in Figure (3).

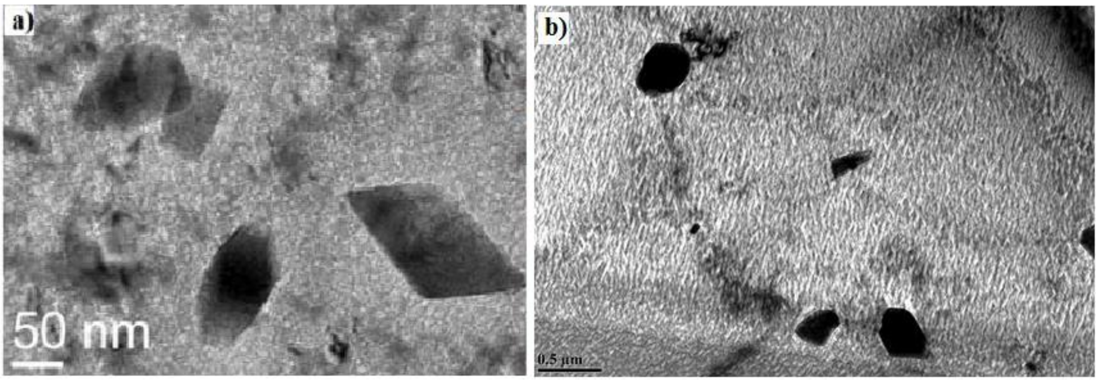

Figure 3: TEM-thin foil analysis shows a presence of Nb precipitates in a) 1Nb alloy annealed at 1200ºC/10 minutes, b) 0.6Nb alloy annealed at 1200ºC/5 minutes.

The same samples which used for AsB analysis were used again for EDX analysis of precipitated particles using SE2 detector with working distance of 13 mm. In order to characterize the sub-micron precipitates, low voltage EDX was carried out to have adequate spatial resolution relative to the size of particles. The resulted EDX spectra of about 40 particles from five images in different areas of each annealed samples showed high peaks of niobium, carbon and nitrogen of the precipitates in all annealed samples of high Nb alloy as shown in Figure (4).

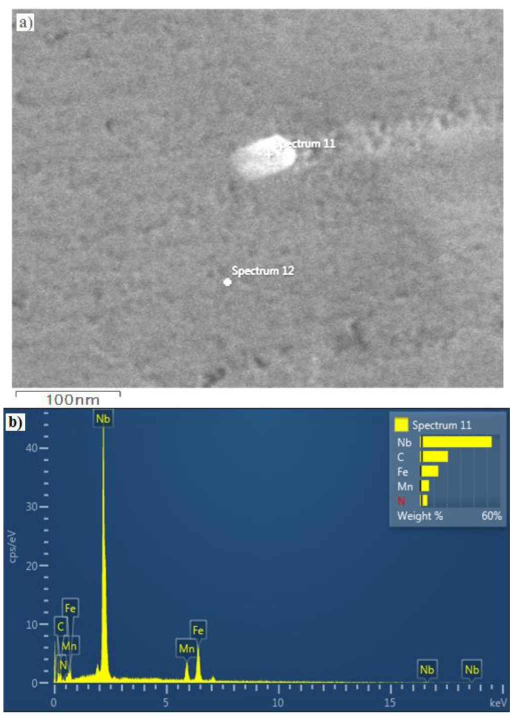

Figure 4: Chemical analysis of precipitated particles a) SEM-AsB of annealed 0.6Nb sample, b) SEM-EDX analysis of the particle shown above.

DISCUSSION

Microstructure

Although, recrystallization behavior is not the aim of this work, fully recrystallized microstructure was seen in Low-Nb group when all samples held for 5 minutes at 1200ºC and grains were fully grown as time was increased. However, for the high-Nb group, fully recrystallized microstructure could not be seen before 10 minutes annealing at 1200ºC. The microstructure behavior has been interpreted as the grain size of Low-Nb group was larger than what was seen for high-Nb samples.

The microstructure investigations of 0.4Nb alloy annealed at 1200ºC for 30 minutes show a grain growth which is evidenced by the absence of any precipitated particles as analyzed by SEM-AsB and TEM. However, low rate of grain growth has been observed in the microstructure of high-Nb alloys. It is possible that the presence of precipitation particles restrains the grain growth of the high-Nb alloy. The SEM-EDX analysis revealed that the precipitated particles were rich in Nb, carbon and nitrogen which is highly suggested to be a Nb(C,N) complex precipitates.

In order to explain the precipitation and solubility behavior of Nb in annealed Fe30Mn samples at 1200ºC/30minutes, theoretical analysis of this case using some references and Thermo-Calc analysis will be used to interpret the microstructure results.

Solubility Products

Sharma et.al [7], studied the solubility products of NbC and NbN in austenite assuming that the activity of carbon and niobium are proportional to their concentrations. They derived theoretical equations for solubility product calculations in the absence of Mn (Equations 1 and 2) and when Mn is present Equations (3 and 4):

$$Log\ [Nb][C] \cong -2.04 - 0.87\left(\varepsilon_C^C X_C + \varepsilon_C^{Nb} X_{Nb}\right) - \left(\varepsilon_{Nb}^{Nb} X_{Nb} + \varepsilon_C^N X_C\right) \quad (1)$$

$$Log\ [Nb][N] \cong -2.55 - 0.87\left(\varepsilon_N^N X_N + \varepsilon_N^{Nb} X_{Nb}\right) - \left(\varepsilon_{Nb}^{NbC} X_{Nb} + \varepsilon_N^{Nb} X_N\right) \quad (2)$$

$$\log[Nb]\,[N] = \{\log[Nb]\,[N]\}_{Mn=0} - (\varepsilon_N^{Mn} + \varepsilon_{Nb}^{Mn})[Mn].\frac{A_{Fe}}{230.3A_{Mn}} \quad (3)$$

$$\log[Nb]\,[C] = \{\log[Nb]\,[C]\}_{Mn=0} - \left(\varepsilon_C^{Mn} + \varepsilon_{Nb}^{Mn}\right)[Mn].\frac{A_{Fe}}{230.3A_{Mn}} \quad (4)$$

Where X_C, X_N and X_{Nb} are the atomic % of the C, N and Nb respectively. The interaction (Wagner interaction) parameters ε_C^N of the C, N and ε_C^{Nb} at 1200oC are shown in Table (2).

Table 2: Wagner interaction for C, N and Nb at 1200ºC [4, 7].

Parameter		Value
ε_C^C	Carbon-Carbon interaction	6.03
ε_N^N	Nitrogen-nitrogen interaction	4.27
ε_C^N	Carbon-nitrogen interaction	3.93
ε_C^{Nb}	Carbon-niobium interaction	-44.98
ε_N^{Nb}	Nitrogen-niobium interaction	-44.98
ε_{Nb}^{Mn}	Niobium-Manganese interaction	-44.1
ε_N^{Mn}	Nitrogen- Manganese interaction	8.85
ε_C^{Mn}	Carbon- Manganese interaction	-4.22

The above equations were used to calculate the NbC and NbN solubility in austenite for all of the studied alloys at 1200ºC as seen in Figure (5). The Figure shows that the NbN has higher stability (less soluble) than NbC, but both have decreased their solubility as Nb increased.

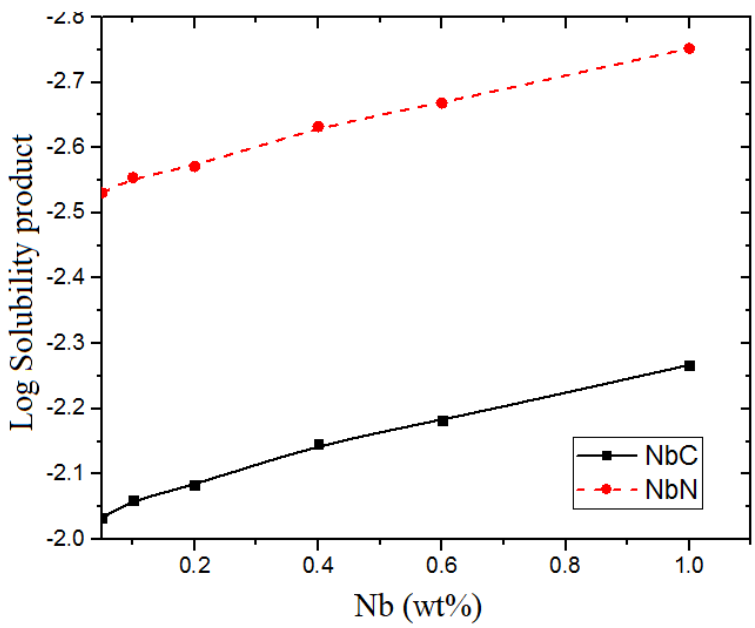

Figure 5: Solubility product of NbC and NbN of the studied alloys at 1200°C in absence of Mn effect.

However, the alloying elements which do not dissolve in austenite such as Mn can also have a significant effect on NbN and NbC solubility as found by Koyama [4], Figure (6).

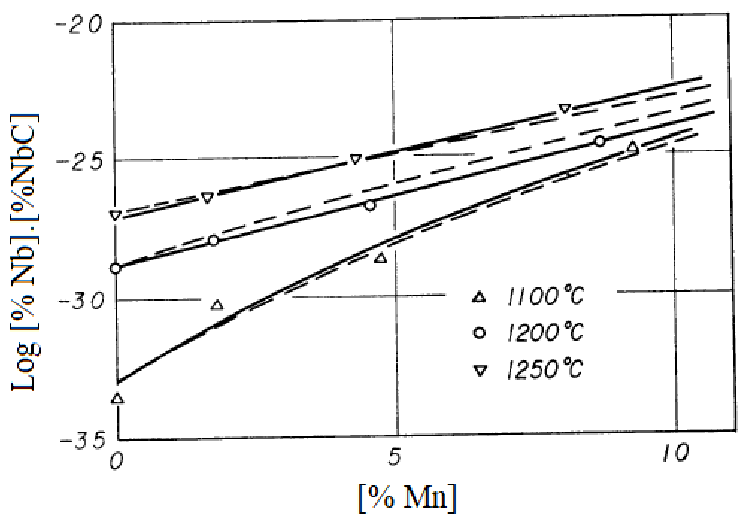

Figure 6: Effect of Mn on the solubility product of NbN in austenite [4].

Applying Koyama's study to calculate the NbN solubility in austenite at a given Nb level by the equation:

$$Log[Nb][N] = -{}^{8500}/_{T} + 2.89 + \left(\frac{1085}{T} - 0.68\right).[Mn] - \left(\frac{48}{T} - 0.032\right)[Mn]^2$$

The solubility results in Figure (7), show that the solubility is slightly increased as Mn increased.

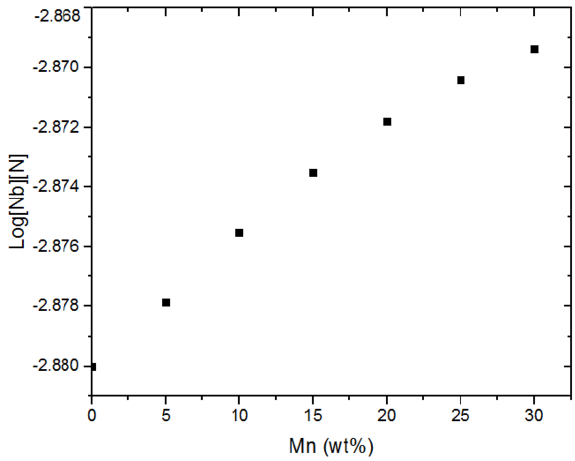

Figure 7: Effect of Mn on NbN solubility of the studied alloys at 1200°C as applied by experimental results of Koyama's study.

Study of Mn effect by Koyama, did not include the Nb effect. Therefore, Sharma [7] equations were used to study the effect of Nb on the NbN and NbC solubility and the results are shown in Figure (8) for 0.05Nb and 1Nb alloys. The Figure shows significant effect of Nb on decreasing of solubility of NbN in austenite. However, this effect is less in NbC solubility products for the same alloy.

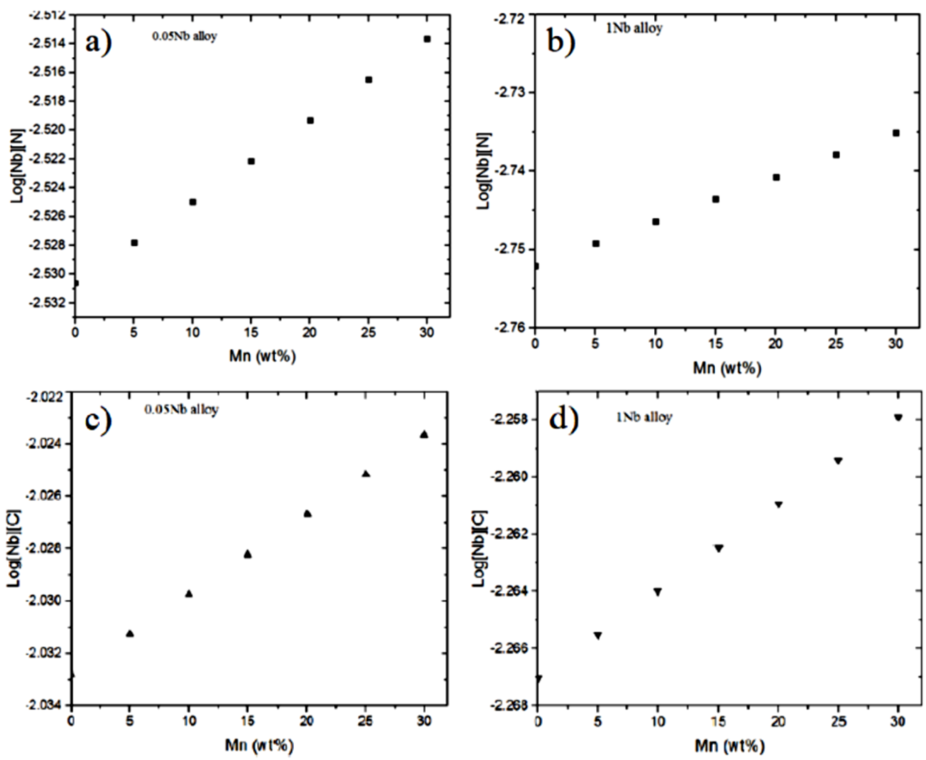

Figure 8: Effect of Mn on NbN and NbC solubility in austenite at 1200°C

At 30 wt.% Mn, the results show that the NbC has higher solubility and this is well matched with references of NbC solubility in austenite reviewed by Sharma [7]. Figure (9) shows the solubility product as a function of temperature. But, this temperature effect is smaller with respect to Koyama's results which could be due to the high Nb content and the fact that Koyama did not study the Mn effect at different Nb contents.

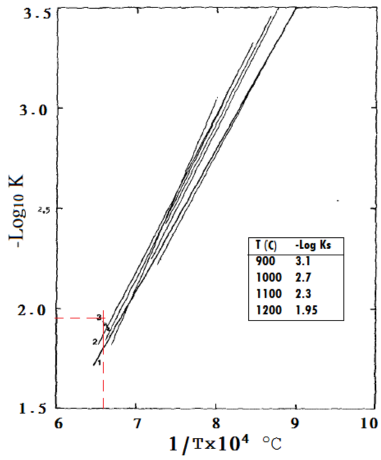

Figure 9: solubility product of NbC in austenite at different temperatures as reviewed from different references by Sharma et.al [5]

Solubility products of the studied alloys show a high NbN stability in austenite at 1200ºC comparing with NbC, this is well agreed with results found by Koyama [4] (Figure 6), although their study was for Mn up to 10 wt.%. However, stability is also affected by Nb content; the results show that the higher is solubility the lower the Nb content. Therefore, NbN or complex phase of Nb(C,N) are expected to be found in the higher Nb alloys. Thermo-Calc software using TCFE8 database, was used to analyze the Nb(C,N) precipitation for the studied alloys at 1200ºC. The results show the effect of Mn on the solubility of Nb(C,N) as shown in Figure (10) and Figure (11).

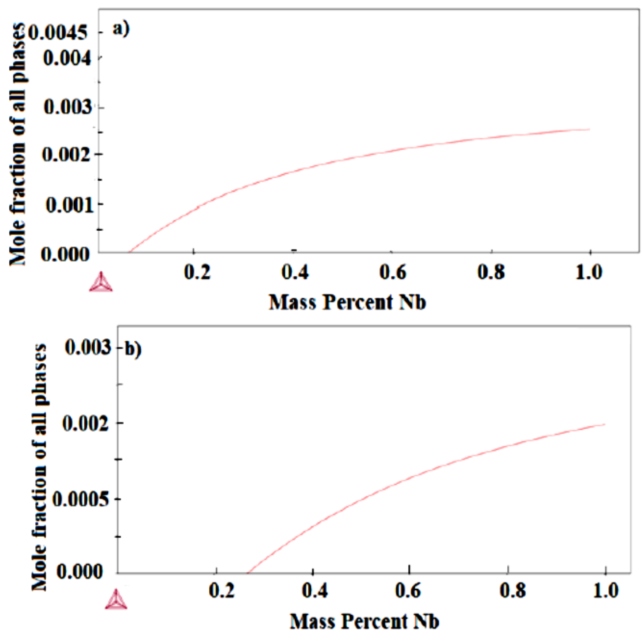

Figure 10: Mole fraction of Nb(C,N) precipitates in the studied alloys annealed at 1200ºC predicted by using TCFE8 database of Thermo-Calc, a) in the presence of 30%Mn, and b) at 1%Mn.

As can be seen from Thermo-Calc analysis that Mn reduces the equilibrium volume fraction of Nb(C,N) for Nb > 0.4 wt%.

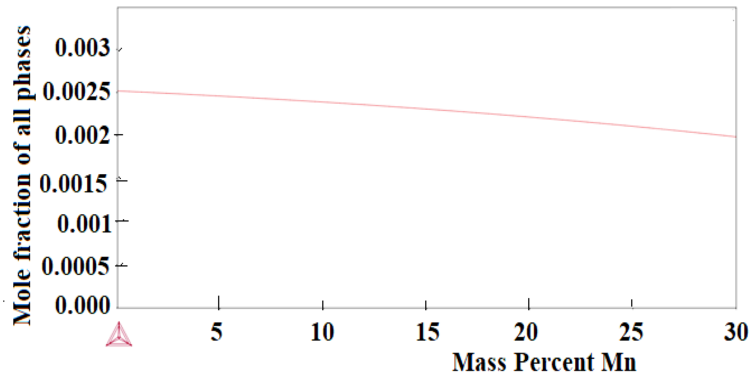

Figure 11: Thermos-Calc estimation of Nb(C,N) volume fraction as a function of Mn content in Fe30Mn1Nb alloy at 1200ºC.

CONCLUSION

The Solubility of Nb in an annealed-high Mn Fe30Mn steel was experimentally investigated and theoretically studied and it has been found that a Complete Nb dissolution is expected in the alloys up to 0.4Nb content and Mn has a moderate effect on Nb solubility in Fe30Mn TWIP alloy. The result was supported by EDX analysis of particles which shows coarse Nb-rich chemical composition with presence of carbon and nitrogen peaks. This will lead to the result that the effect in this case is expected to be a solute drag effect. But the high percentage of the detected coarse precipitates were expected to be residual from previous sample processing and are not expected to significantly retard grain growth. The difference in the carbon content between the two alloy groups due to the conventional casting might be effect this result therefore, vacuum casting that can control carbon content and get ultra-low carbon in Nb-Fe30Mn alloys is recommended.

REFERENCES

[1] Scott, C., et al., "The development of a new Fe-Mn-C austenitic steel for automotive applications" Revue de Métallurgie, 103 (06), 2006 page. 293-302.

[2] Aidang, S. and F. Liming, "Effect of nb solute drag and nbc precipi-tate pinning on the recrystallization grain growth in low carbon nb-microacloyed steel". Acta Metallurgica Sinica, 2010. 46 (7) 2010 page 832.

[3] Medina, S., M. Gómez, and P. Gómez, "Effects of V and Nb on static recrystallisation of austenite and precipitate size in microalloyed steels". Journal of Materials Science, 45(20) 2010 page 5553-5557.

[4] Koyama, S.I., T.; Narita, K., "Effects of Mn, Si, Cr, and Ni on the reaction of solution and precipitation of niobium nitride in iron austenite" J. Jap. Inst. Metals, 35(7) 1971 pp 698-705.

[5] Bouaziz, O., et al., "High manganese austenitic twinning induced plasticity steels: A review of the microstructure properties relationships" Current Opinion in Solid State and Materials Science, 15(4) 2011 page 141-168.

[6] Bouaziz, O., et al., "Effect of chemical composition on work hardening of Fe-Mn-C TWIP steels" Materials Science and Technology, 27(3) 2011 page 707-709.

[7] Sharma, R., V. Lakshmanan, and J. Kirkaldy, "Solubility of niobium carbide and niobium carbonitride in alloyed austenite and ferrite" Metallurgical and Materials Transactions A, 15(3) 1984 page 545-553