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QUANTIFICATION OF NANO-SIZED PRECIPITATES IN MICROALLOYED STEELS BY MATRIX DISSOLUTION

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ABSTRACT

Microalloyed steels possess good strength, toughness and excellent weldability, all of which are necessary attributes for oil and gas pipelines in northern climates. These properties are attributed in part to the presence of nano-sized Nb/Ti carbide precipitates. In order to understand the strengthening mechanisms and to optimize the strengthening effects, it is necessary to quantify the size distribution, volume fraction and chemical speciation of these precipitates. However, characterization techniques suitable for quantifying fine precipitates are limited. A matrix dissolution method has been developed to extract the nano-sized precipitates from microalloyed steels. The results from Grade 100 microalloyed steel are presented in this paper.

INTRODUCTION

It is known that the combination of microalloying additions, such as Nb, Ti and V, to the steel and controlled rolling can enhance the strength and ductility of steel. The improvement of mechanical properties results from the refinement of ferrite grain size, precipitation, solute strengthening and dislocation strengthening. The first three can be expressed mathematically as follows: [1]

$$\sigma_y(MPa) = \sigma_i + k_y\, d^{-1/2} + \left(\frac{10.8 v_f^{1/2}}{X}\right)\ln\left(\frac{X}{6.125*10^{-4}}\right) + \sum k_i C_i$$

(1)

where:

σ_y is the yield stress,

σ_i is the friction stress of iron,
k_y is the strengthening coefficient for grain size,
d is the grain diameter in microns,
X is the size of precipitates in microns,
v_f is the volume fraction of a given precipitate size (X),
k_i is the strengthening coefficient for solute strengthening of solute i and
C_i is the concentration of solute i.

Precipitates of different sizes contribute to each of these strengthening mechanisms in various ways. In order to maintain a fine austenite grain size prior to transformation, particles that precipitate in austenite, or particles that will precipitate during hot rolling are required. They retard recrystallization, resulting in a high recrystallization temperature. Deformation in the recrystallization region will assist in the formation of fine ferrite grains, [2] producing dislocation strengthened forms of ferrite, [3] and strain-induced precipitation. These precipitates, typically carbides, nitrides and/or carbo-nitrides of Nb, Ti, and V, are >20nm in size. [4,5]

In order to produce dispersion strengthening, very fine particles (<20nm) are needed. [6] These nano-sized precipitates form during or after transformation from austenite to ferrite and are the most important for dispersion strengthening. For a given volume fraction, refinement of particle size can produce a significant increase in yield stress.

Therefore, quantitatively determining the volume fraction of all precipitates is critical to understanding the relationship between strengthening and processing history in microalloyed pipeline steels. However, the small particle sizes and low volume fractions make it very difficult to quantify the volume fraction by conventional methods.

Conventional metallographic methods - imaging

Microscopic methods are commonly used for identifying, locating and characterizing precipitates. Both optical microscopy and scanning electron microscopy (SEM) have limited resolution. Transmission electron microscopy (TEM) has superior imaging resolution and spatial resolution for energy dispersive x-ray (EDX) analysis. Electron diffraction techniques can also provide valuable crystallographic information, which is instrumental in identifying specific precipitates. When it comes to precipitate quantification, TEM analysis does have limitations because TEM specimens are either thin foils or extraction replicas. The limitations are a direct result of the specimens utilized. First, there is the issue of whether the sample examined is representative of the bulk material. Second, quantification may be in error because of particle overlap. [7] Third, for thin foil samples, particles may intersect the thin foil surface. If the particle center is outside the foil sample, the particles are partially removed or may be attacked by the polishing agent during the sample preparation process and consequently show a smaller radius. [7,8] Finally, determination of the volume fraction of the precipitates depends on the accurate determination of the thin foil thickness or, for replicas, the sample thickness from which the particles were extracted. Neither value is straight forward to determine. Other microscopic methods, such as scanning transmission electron microscopy (STEM), atomic-force microscopy (AFM) and field ion microscopy (FIM) with atom probing (AP) also provide high resolution analysis, but suffer from many of the above limitations as well as others. Therefore, microscopic methods are not completely satisfactory for quantifying precipitate volume fractions.

Small-angle neutron scattering (SANS) - magnetic measurements

Small-angle neutron scattering (SANS) can be used to measure the size and volume fraction of nano-sized precipitates. The size range of conventional SANS is approximately 2 nm to 100 nm. With this method, a larger volume of material is used because of the greater penetration depth of neutrons. The ferromagnetic matrix is magnetized to saturation and scattered neutrons are recorded. Because the precipitates are non-magnetic, they can be treated as "magnetic holes" in the ferromagnetic matrix. Therefore, precipitate size distribution and volume fraction of the precipitates can be obtained from the magnetic cross section. [9] This method cannot distinguish between different types of precipitates; only the size distribution of all precipitates is measured. An additional technique, such as XRD or TEM, must be used to identify specific types of precipitates.

Matrix dissolution techniques

The matrix dissolution method is a very promising technique to quantify precipitates. Relatively large volumes of material are analyzed, so that statistically significant quantities of precipitates of different sizes are collected. Particles can be specifically identified after extraction. There are three important steps for this method. First, the steel matrix is dissolved. Next, the precipitates can be isolated by centrifuging or filtering. Filtering is widely used to extract micron-sized particles. Centrifuging is a better choice to collect submicron precipitates. Finally, once the precipitates are collected, phase identification is done by either XRD or TEM.

Matrix dissolution can be classified into chemical dissolution and electrolytic dissolution. [10,11,12] Chemical dissolution can be further classified into acid dissolution and halogen-based mildly alcoholic solution dissolution. [10]

For acid dissolution, various acids, such as HCl, H_2SO_4, HNO_3, have been reported in the literature to extract different particles. Only those phases stable in acids, such as silica, alumina, [10] and some carbides and nitrides,

have been successfully extracted. Unstable phases, such as MnS and Fe$_3$C, were not extracted, as reported by W. R. Bandi [13] and verified by our own experiments. HCl can be used to extract insoluble precipitates, such as Ti and Nb carbo-nitrides, from steel. The reaction product FeCl$_2$ from the reaction of Fe and HCl, is soluble in HCl, H$_2$O and ethanol. Therefore, it is possible to remove FeCl$_2$ from the solution, leaving insoluble particles.

Halogen-based separation is perhaps the oldest dissolution technique. Because Br$_2$ and I$_2$ have good solubility in some organic solvents, there are several chemical combinations: bromine in methanol or ethanol, iodine in methanol or ethanol and iodine-methanol-methyl acetate. I$_2$ solution is mainly used to isolate chemically unstable phases such as Fe$_3$C, MnO, MnS [14] and FeS. [13] It also has been used to isolate carbides such as Cr$_2$C, Cr$_7$C$_3$, and Cr$_{23}$C$_6$. [13] It is generally considered that treatments with Br$_2$ and nonaqueous solvents are the best methods for separating stable oxides (Al$_2$O$_3$, Cr$_2$O$_3$, Fe$_2$O$_3$, FeO, ZrO, etc.) and nitrides (AlN and ZrN) from steel. [13,15] These Br$_2$ mixtures should not be used for separation of carbides because too many carbides dissolve, leaving a residue of amorphous carbon.[13,16]

Electrolytic dissolution is a selective dissolution process, during which an anode and cathode are suspended in a cell with an electrolyte. The steel sample works as the anode. With the combination of the electrolyte and either an applied voltage or current, the steel matrix is dissolved while the second phases are retained as a residue. Electrochemical methods are more complex than chemical dissolution methods. The dissolution parameters, such as current, potential, pH, temperature and other cell parameters, need to be closely controlled.

Since the precipitates of interest range in size from several microns down to less than 5 nm, microscopic techniques alone are not suitable for quantifying the size, size distribution and volume fraction of precipitates in steels. SANS and matrix dissolution techniques offer opportunities to provide quantitative information based on samples that are more representative of the steel strip. Stable Ti and Nb carbo-nitrides are the focus of this study. Chemical dissolution using HCl combined with centrifugal separation is explored for Grade 100 microalloyed steel. TEM and other techniques are used in a complementary manner to fully identify and characterize precipitates.

EXPERIMENTAL PROCEDURE

Grade 100 microalloyed steel, supplied by IPSCO Inc., was used in this study. The composition is given in Table I. The dissolution and extraction procedure is summarized in the flow chart shown in Figure 1.

Table I Chemical Composition of Grade 100 Microalloyed Steel (wt %)

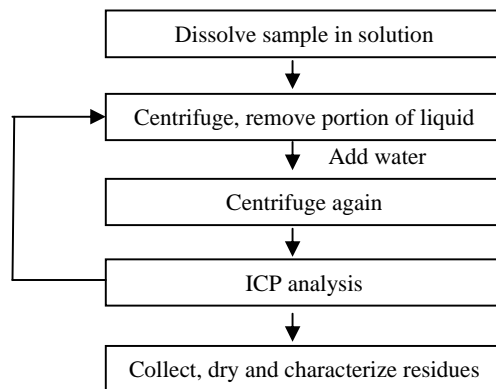| Element	C	Mn	Si	V	Nb	Mo
wt %	0.080	1.800	0.244	0.047	0.094	0.301
Element	Ti	N	Cu	Al	Cr	Ca
wt %	0.06	0.011	0.42	0.05	0.197	0.005

Figure 1: Dissolution procedure.

The chemical dissolution method was used to extract the Ti and Nb carbo-nitrides. HCl acid solution (a 1:1 mixture by volume of HCl acid with a specific gravity 1.19 and distilled water) was used at 65-70°C under two conditions: open to air and bubbling N$_2$. An amorphous Si-O phase (likely SiO$_2$) was identified in the residues for both conditions. Dilute HF was used to dissolve the SiO$_2$.

A centrifuge was used to separate solid particles from the solution by rapidly rotating the material up to 40,000 RCF (Relative Centrifugal Force) at 4°C. ICP (inductively-coupled plasma) spectroscopy was used to analyze the concentration of the elements in the solution after centrifuging, as a means of performing a mass balance. The purpose of diluting the solution and repeating the centrifuging was to remove the Fe ions (in the form of FeCl$_2$) from the solution. Centrifuging was stopped when the solution became transparent and colorless or

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when the concentration of Fe was very low. Iron levels were checked by ICP or AAS (atomic absorption spectroscopy). An analytical balance with an accuracy of 0.1 mg was used to measure the weight of the sample before dissolution and the weight of the extracted residues.

Composition analysis of the extracted residues was provided through EDX analysis in the SEM (Hitachi S2700). Phase identification was done through a Rigaku Geigerflex 2173 X-ray Diffractometer (XRD) equipped with a Co source. Precipitates were also collected on carbon coated 300 mesh Cu grids for TEM examination to identify specific types of precipitates. The grids were examined in a JEOL 2010 TEM, equipped with EDX detector, operated at 200 kV.

RESULTS AND DISCUSSION
Microstructure
The overall microstructure of the Grade 100 steel was mainly bainitic ferrite, as shown in Figure 2. Details of the microstructure have been discussed elsewhere. [17]
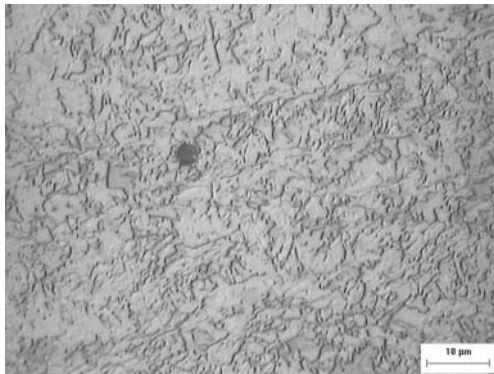
Figure 2: Optical microscope image of Grade 100 microalloyed steel.

Preliminary results of the extracted residues are presented. Further work is needed to quantify the volume fraction of the precipitates.

EDX analysis by SEM
Figure 3 shows an SEM EDX spectrum of the extracted residue from a solution exposed to air. Several elements, i.e., Ti, Nb, Mo, Fe, Cl, Si, and O are present in the residue. Nb, Ti, Mo come from the precipitates. Fe and Cl arise from the incomplete removal of Fe ions from the solution.
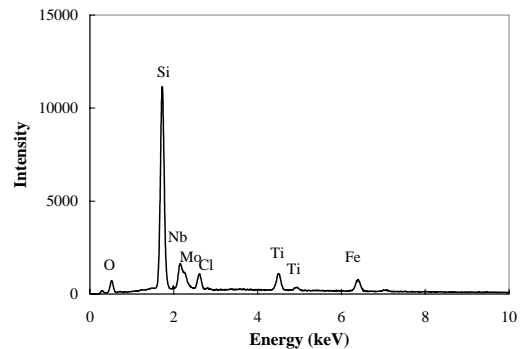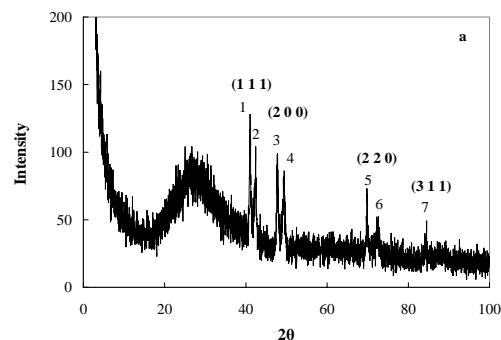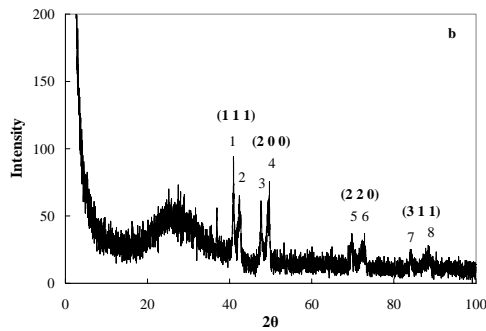

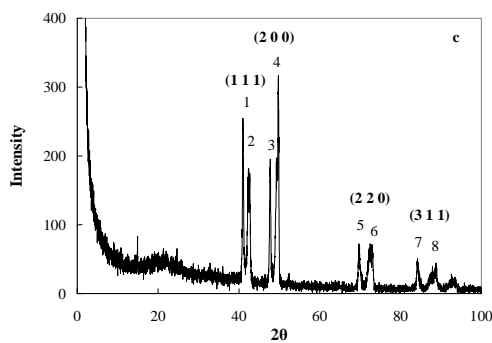Figure 3: EDX spectrum of extracted residue.

XRD analysis
Figure 4 shows XRD spectra of residues extracted from Grade 100 microalloyed steel under different conditions. Because the crystal structure (NaCl-type structure) and lattice parameters of the precipitates are similar and vary with composition, it is difficult to differentiate the carbides, nitrides and carbonitrides of the microalloying elements. Only the Miller indices are shown in Figure 4. The residues are primarily Ti and Nb carbo-nitrides. Peaks 1, 3, 5 and 7 are from Nb-rich precipitates; the others are from Ti-rich precipitates. A broad peak was observed between 20° and 30° (2θ), shown in Figure 4a and 4b, and to a lesser extent in Figure 4c, which indicates the presence of an amorphous phase in the residues. This peak is likely the Si-O phase mentioned previously. After HF treatment, the amorphous phase was mostly removed, which accounts for the much less intense peak in Figure 4c.

a) XRD spectrum from extracted residue – solution open to air.

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b) XRD spectrum from extracted residue -
solution exposed to bubbling N_2.

c) XRD spectrum from extracted residue -
solution exposed to bubbling N_2 and then residue
treated with HF.

Figure 4: XRD spectra from residues extracted
from Gr100 steel using HCl solution.

TEM analysis

Figure 5 shows an example of a TEM bright
field (BF) image and EDX spectra from Nb-rich
precipitates attached to a Ti-rich precipitate
extracted by the HCl method. The Nb-rich
particles have grown epitaxially on the Ti-rich
particle. Because TiN has a lower solubility in
Fe (either austenite or ferrite) than NbC, NbN or
Nb carbo-nitrides, it precipitates first in the steel
on cooling and can act as nucleation sites for
Nb-rich precipitates as shown in Figure 5a.
Although there is likely C present in the residue,
the large C peak arises primarily from the carbon
coated Cu grid. The Cu peak arises from the Cu
grid. The small Fe peak is from the matrix; Fe
ions were not fully removed from the solution.
The Si and O peaks (Figure 5c) are from the
amorphous Si-O phase still present in the residue.
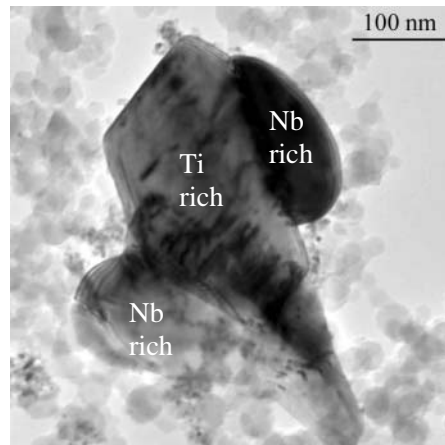
a) TEM BF image of Nb-rich precipitates
attached to a Ti-rich precipitate.
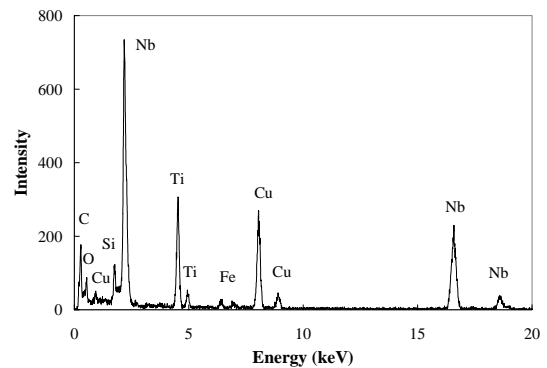
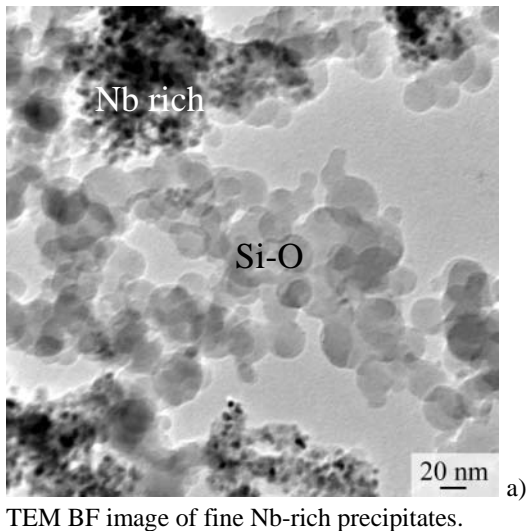b) EDX spectrum from top Nb-rich precipitate in
(a).
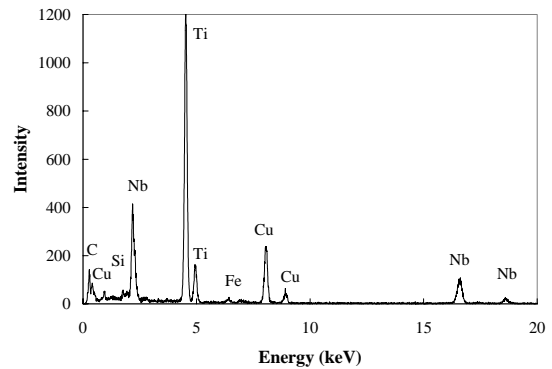
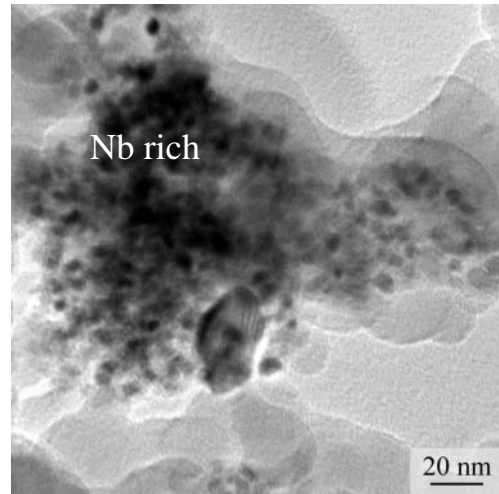c) EDX spectrum from Ti-rich precipitate in (a).

Figure 5: TEM BF image and EDX spectra from
Nb-rich precipitates attached to a Ti-rich
precipitate.

The finest precipitates extracted by the HCl
method are less than 5nm in size (Figure 6a and
6b). EDX spectra from these fine particles
(Figure 6c) reveal that they are Nb- and Mo-rich,

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and contain Ti and V. An amorphous Si-O phase (Figure 6d), seen as spherical particles in Figure 6a, was also present in the residue. This phase is likely responsible for the broad peak in the XRD spectra. The amorphous Si-O phase is also present in the residues when N_2 is bubbled through the HCl solution during the matrix dissolution process. This is an indication that the source of O is the steel and not the solution. Silicon is also present in the steel, either in solid solution in the Fe matrix or as oxide/silicate inclusions. After steel dissolution, Si likely combined with the O to precipitate SiO_2. Silica was also found by other researchers in their extraction residues. [11], [14], [15], [18], [19], [20] Okura extracted SiO_2, along with Al_2O_3, MnO and FeO with alcoholic-iodine and bromine solutions.
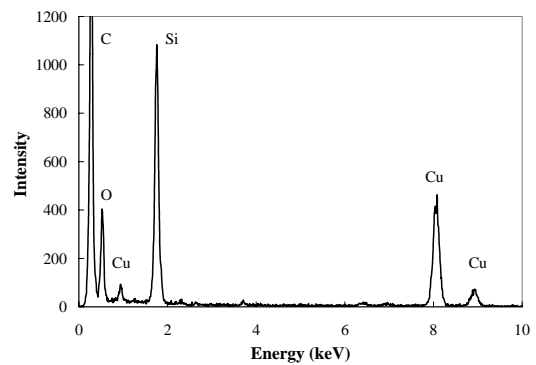

b) TEM BF image of fine Nb-rich precipitates.

c) EDX spectrum from Nb-rich precipitates.
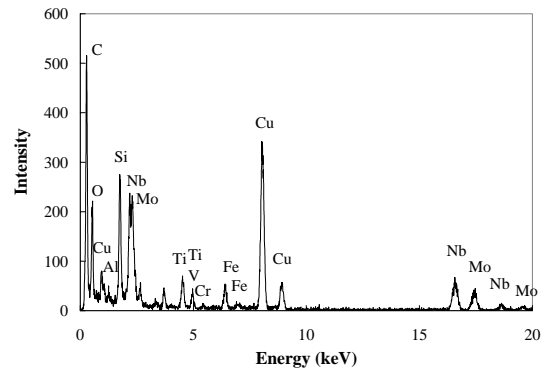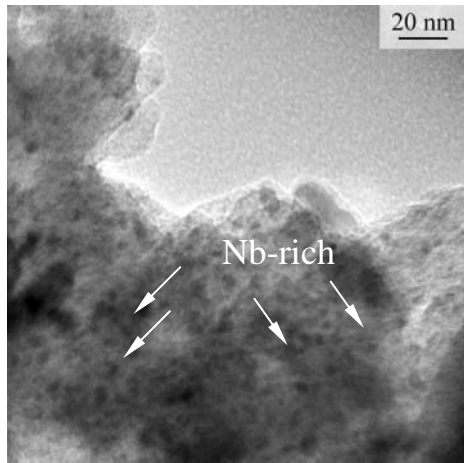

TEM BF image of fine Nb-rich precipitates.

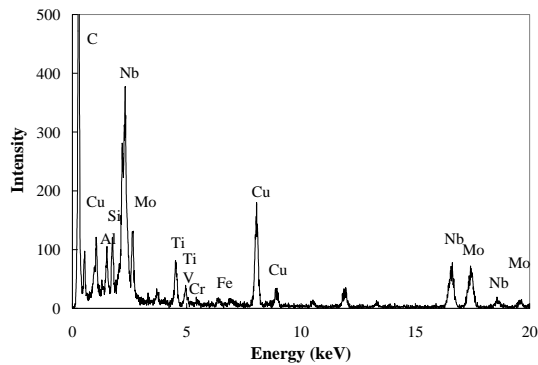d) EDX spectrum from Si-O phase.

Figure 6: TEM BF images and EDX spectrum from fine particles extracted using HCl solution, open to air.

In an attempt to dissolve the Si-O phase, dilute HF (<1%) was used after extraction and the centrifuging process was repeated. Figure 7

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shows a TEM image and an EDX spectrum from the fine Nb-rich precipitates. Most of the SiO_2 phase had been removed.

a) TEM BF image of the precipitates after HF treatment.

b) EDX spectrum from Nb rich precipitates.

Figure 7: TEM BF image and EDX spectrum from fine precipitates after HF treatment.

Mass balance

After the precipitates had been extracted from the HCl solution, ICP analysis was performed on the centrifuged solution. By comparing the chemical composition of the steel with the ICP analysis of the solution, the amount of the element extracted from the steel as part of the residue was obtained, as shown in Table II. Most of the Si in the steel matrix was present in the residue as SiO_2. Most of the Nb and Ti in the steel was in precipitate form, while approximately half of the V precipitated out and most of the Mo was dissolved in the ferrite matrix.

Table II Percentage of Elements Extracted from Grade 100 Steel in Particle Form

Element	Si	Ti	Nb	V	Mo
%	95.9	77.1	91.0	50.0	18.2

The relative extraction yield of the microalloying elements can partially be explained by comparing the solubility differences of the microalloying elements and their carbides, nitrides and carbo-nitrides. Among Ti, Nb, V and Mo, V has the highest solubility in ferrite and austenite. Vanadium carbo-nitrides have a much higher solubility in ferrite and austenite as well, compared with the solubility of other microalloy carbo-nitrides. The solubility of VN is about two orders of magnitude smaller than VC. [6] This is why V is a common choice for controllable precipitation strengthening in steels. This also accounts for the fact that much of the V does not precipitate and remains dissolved in the steel matrix during the steel processing, accounting for the low extraction yield of V carbo-nitrides. The other reason to explain the low yield for V and Mo is that V and Mo carbides form in ferrite while Nb and Ti precipitate significantly in austenite. Accelerated cooling of these steels will suppress precipitation of V and Mo carbides.

Precipitation information obtained by EDX, XRD and TEM are consistent with each other, which indicates that Nb and Ti precipitates, especially the fine Nb- rich precipitates, have been successfully extracted by HCl dissolution combined with centrifuging. Further work is needed to separate different sized precipitates and then to quantify their volume fractions. Filtration, with membranes of different pore sizes (as small as 10 nm), will be utilized. SANS tests will also be used as a complementary method to verify the volume fractions of the various precipitates.

SUMMARY
1) The matrix dissolution method is a promising technique for quantifying precipitates in microalloyed steels.
2) Preliminary results showed that HCl acid is capable of successfully extracting Ti and Nb carbo-nitrides from a microalloyed steel.
3) The precipitates collected have different sizes, including very fine precipitates (<5nm). Filtration methods are suggested to further separate the different sized

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precipitates and then to quantify the volume fractions of fine precipitate in microalloyed steels.

4) The precipitate information obtained by different analyses are consistent each other and also consistent with that from carbon replicas by other researchers.

5) Silicon, present in solution in ferrite and as oxide and silicate inclusions, dissolves in the HCl solution and precipitates out as amorphous SiO_2. Most of the SiO_2 can be removed with dilute HF acid.

ACKNOWLEDGEMENTS

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