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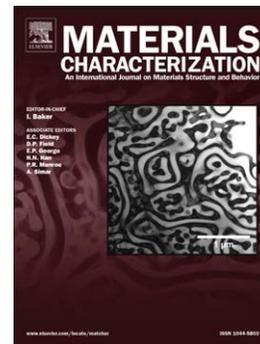
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Roghayeh Mohammadzadeh, Alireza Akbari

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Grain refinement of a nickel and manganese free austenitic stainless steel produced by pressurized solution nitriding

Roghayeh Mohammadzadeh¹, Alireza Akbari²

Faculty of Materials Engineering, Sahand University of Technology, P.O. Box 51335-1996, Tabriz, Iran.

Abstract

Prolonged exposure at high temperatures during solution nitriding induces grain coarsening which deteriorates the mechanical properties of high nitrogen austenitic stainless steels. In this study, grain refinement of nickel and manganese free Fe-22.75Cr-2.42Mo-1.17N high nitrogen austenitic stainless steel plates was investigated via a two-stage heat treatment procedure. Initially, the coarse-grained austenitic stainless steel samples were subjected to an isothermal heating at 700 °C to be decomposed into the ferrite+Cr₂N eutectoid structure and then re-austenitized at 1200 °C followed by water quenching. Microstructure and hardness of samples were characterized using X-ray diffraction, optical and scanning electron microscopy, and micro-hardness testing. The results showed that the as-solution-nitrided steel decomposes non-uniformly to the colonies of ferrite and Cr₂N nitrides with strip like morphology after isothermal heat treatment at 700 °C. Additionally, the complete dissolution of the Cr₂N precipitates located in the sample edges during re-austenitizing requires longer times than 1h. In order to avoid this problem an intermediate nitrogen homogenizing heat treatment cycle at 1200 °C for 10 h was applied before grain refinement process. As a result, the initial austenite was uniformly decomposed during the first stage, and a fine grained austenitic structure with average grain size of about 20 μm was successfully obtained by re-austenitizing for 10 min.

Keywords: High nitrogen austenitic stainless steel; Solution nitriding; Grain refinement; Homogenizing; Chromium nitride.

¹ E-mail address: r_mohammadzadeh@sut.ac.ir

² Corresponding author: E-mail address: akbari@sut.ac.ir , Tel: +98411-3459416 Fax: +98411-3444333

1. Introduction

Nitrogen has been successfully used as an inexpensive alloying element to develop commercial high nitrogen austenitic stainless steels (HNASSs) with high strength and high corrosion resistance [1-4]. Nitrogen is a strong austenite stabilizer and therefore, it can be used as substitute for the expensive nickel. Additionally, the nickel contained in the conventional medical stainless steels (for example AISI 316L grade) causes allergy problems in the human body. Therefore, production of nickel free HNASSs offers a new perspective on development of more efficient metallic biomaterials [5-8]. During last decades, different grades of Fe-Cr-Mn-Mo-N [9-12], Fe-Cr-Mn-N [13, 14] Ni-free HNASSs have been developed as new biomedical steels. These high nitrogen stainless steels are produced by high pressure melting under nitrogen atmosphere and contain large amount of chromium (15-25 wt. %), manganese (10-24 wt. %) and nitrogen (0.45-1.1 wt. %). However, recent studies in cytotoxicity evaluation of metal salts using murine fibroblasts and osteoblastic cells have indicated rather high toxicity of manganese and their salts [15, 16]. Thus, more recently nickel and manganese free (Ni- and Mn-free) austenitic stainless steels have drawn attention as harmless biomaterials [17].

Recently, solution nitriding (also called high temperature gas nitriding) was recognized as a versatile, simple and promising solid state manufacturing process for fabrication of the high nitrogen stainless steels. The process, which was initially introduced by Berns et al. [18], runs out at high temperatures above 1050 °C under nitrogen gas atmosphere. Using this process, it is possible to achieve up to 2.5 mm nitrided depths on stainless steels [19-22]. This enables the process to be used for nitriding the whole thin sections. Thin sectioned components could be fabricated into their final shape in the ferritic state and then austenitized using solution nitriding process. Therefore, nickel and manganese free austenitic stainless steel plates, small devices and foils with high strength and corrosion resistance can be fabricated by nitriding the Ni- and Mn-free ferritic stainless steel under N₂ gas at 1000-1200°C without requiring any special equipment.

However, prolonged exposure at high temperatures during solution nitriding process results in the formation of coarse-grained austenite with inferior mechanical properties. This unfavorable effect becomes more important with increasing the sample thickness. On the other hand, most of the Ni- and Mn- free HNASSs (including Fe-25Cr-1.1 N [23], Fe-24Cr-N and Fe-24Cr-2Mo-N [24] and Fe-22.75Cr-2.42Mo-N [25] steels) are inherently susceptible to inter-granular brittle fracture in tensile testing at ambient temperature. The research studies performed using Vickers indentation tests [25] and Transmission Electron Microscopy (TEM) [23] imply that the inter-granular brittle fracture is closely related to activation of straight slip bands and formation of pile ups with planar array of dislocations at the grain boundaries. To suppress inter-granular fracture, the stress concentration exerted by planar array of dislocations at the grain boundaries should be decreased. Therefore, application of a subsequent grain refinement process was proposed as a route to achieve this purpose.

The common process of grain refinement via plastic deformation cannot be applied on Ni- and Mn-free HNASSs due to low ductility despite of having Face Centered Cubic (FCC) structure [25, 26]. In contrast, the phase diagram of the Ni- and Mn-free HNASSs predicts a heat treatment route for austenite grain refinement. When Ni- and Mn-free high nitrogen austenite is isothermally heated below the austenitizing temperature, it becomes unstable and decomposes to ferrite and chromium nitride (i. e. $\gamma \rightarrow \alpha + \text{Cr}_2\text{N}$). If fully decomposed high nitrogen austenitic steel is again reheated to the austenitizing temperature and held for a sufficient time, the structure will transform to austenite. As many nucleation sites are available, the size of the new austenite grains will be small.

The production of the nickel and manganese free austenitic stainless steels by solution nitriding has many advantages and is regarded as promising route. However, more investigations are needed to be done in order to overcome the grain coarsening and brittle fracture problems and also to deeply understand the austenite grain refinement process. It seems that post grain refinement treatment is an useful way to improve the tensile properties and fracture toughness. The present study is aimed at investigating the grain refinement of a Ni- and Mn-free Fe-22.75Cr-2.42Mo-1.17N austenitic stainless steel plates, produced by solution nitriding at 1200°C in a nitrogen gas atmosphere under pressure of 0.25 MPa. The austenite grains were refined by a two-stage isothermal (decomposition–re-austenitizing) heat treatment procedure. To achieve successful grain refinement, a homogenization pre-heat-treatment was applied and its effects on grain refinement process of the steel was investigated and discussed.

2. Experimental procedure

Nickel and manganese free Fe-22.75Cr-2.42Mo-1.17N austenitic stainless steel plates with 2 mm thickness were produced by solution nitriding at 1200 °C under nitrogen gas pressure of 0.25 MPa. The Fe-Cr-Mo alloy was prepared by induction melting in an argon atmosphere followed by electroslag remelting and homogenizing at 1100 °C for 48 h. Table 1 indicates the chemical composition of the investigated Fe-Cr-Mo steel in this research. The initial ferritic plates were prepared by hot rolling of a 10 mm thick slab at 1000 °C. The plates were annealed at 900 °C for an hour before solution nitriding.

Nitrogen was added to ferritic stainless steel plates by solution nitriding in horizontal tube furnace. Samples were ultrasonically cleaned successively in acetone and ethanol and were located in the AISI 304 steel stages before high temperature gas nitriding process. The air in the furnace was purged with nitrogen for 15 minutes to prevent oxidation of the samples. After the purging was completed, the heating procedure at 10 °C/minute was started and nitrogen gas was introduced into the furnace continuously. When the temperature reached 1200 °C, the pressure of nitrogen gas raised to maintain a pressure of 0.25 MPa (2.5 bar) in the furnace. Finally, the nitrided specimens were water quenched. The optimum full nitriding time was obtained based on

the solution nitriding at different times of 1, 3, 6, 9, 12, 13, and 18h. At prolonged nitriding times, chromium nitride precipitates are formed via a discontinuous precipitation mechanism [25].

Coarse grains of the as-solution-nitrided steel were refined by a two-stage isothermal heat treatment procedure. Microstructural investigations were performed using optical microscopy (OM, Olympus-PMG3) and scanning electron microscopy (SEM, JSM-5900 operated at 20 kV). The polished surface was chemically etched in modified aqua regia (50 % HCl-25 % HNO₃-25% H₂O (Vol. %)). Phase composition of the samples were studied by X-ray diffraction (XRD) using a Bruker D8 advanced diffractometer operated at 40 kV and 40 mA with the Cu-K_α radiation ($\lambda=1.5406 \text{ \AA}$) in the Bragg-Brentano configuration. XRD patterns were recorded with step size of 0.05° and step durations of 2 seconds at each step in the angular range of 40°-100°.

The average nitrogen content in the ferritic and austenitic samples was measured using a LECO TN500 nitrogen determinator in a self-contained electrode furnace for fusion. In this method the nitrogen content is determined by measuring the thermal conductivity of the nitrogen containing gas in a Thermal Conductivity (TC) cell. The cross-sectional hardness was investigated using MDPEL-M400 GL microhardness tester equipped with a Vickers indenter. Micro-hardness measurements were performed under the loads of 100 and 500 g applied for 15 s on the mechanically polished and cleaned surfaces.

In the following, the as solution nitrided, homogenized, and grain refined steel samples are denoted with SN-12H, SN-12H-H and SN-12H-R, respectively.

3. Results and discussion

3.1. Phase transformation of ferrite to austenite by solution nitriding

Typical optical micrographs of the ferritic steel plate before and after solution nitriding are presented in Fig. 1. The cross-sectional microstructure of base material before solution nitriding (Fig. 1a) consisted of equiaxed ferrite grains with the average grain size of about 130 μm . As the initial plate was subjected to hot rolling followed by annealing at 900 °C, it is likely that this structure has been developed due to the static re-crystallization during annealing. After solution nitriding for a sufficient time, the ferritic structure was transformed completely to the austenitic structure throughout the plate thickness (Fig. 1b). It is observed that high temperature solution nitriding for long time resulted in coarse austenite grains (several hundred micrometers). Some twins are also present in Fig. 1b (indicated by arrows). As the initial ferritic structure was free from twins, these twins have been produced due to the nitrogen absorption during solution nitriding.

Fig. 2 represents the X-ray diffraction patterns taken from surface of the steel samples before and after solution nitriding. The XRD patterns show the ferrite phase (α) for nitrogen free steel and development of single-phase austenitic structure (γ) for nitrogen containing steel. No chromium nitride phases (Cr_2N and CrN) were detected in the as-solution-nitrided samples by XRD analysis.

The total nitrogen contents of the initial ferritic and solution nitrided (austenitic) samples are given in Fig. 3. Analysis of the intensity-time curves shown in Fig. 3, gives an average bulk nitrogen concentrations of 0.02 wt. % and 1.17 wt. % for initial ferritic and austenitic steels, respectively. This indicates that the initial ferritic steel has absorbed more than 1 wt. % nitrogen which is sufficient to transform it to austenite phase.

3.2. Austenite grain refinement by isothermal heat treatment

According to the Fig. 1b, the as-solution-nitrided sample exhibits non-uniform microstructure and coarse grains. This can deteriorate the mechanical properties of as-produced HNASS. In order to obtain a more uniform microstructure and to improve mechanical properties; the austenite grains were refined via a two-stage isothermal heat treatment procedure. The Fe-Cr-Mo-N phase diagram provides the basis for austenite grain refinement by heat treatment. According to the calculated phase diagram of Fe-22.75Cr-2.42Mo-(2-3)N shown in Fig. 4, in the temperature range of 25-1000 °C, the ferrite (α) and chromium nitride (Cr_2N) phases are stable and at temperatures above 1080 °C the austenite is the equilibrium phase.

Following Fig. 4 it seems that grain refined austenite can be produced by a two-stage heat treatment procedure; (i) isothermal heating of the coarse-grained austenitic steel below 1000 °C to be decomposed to ferrite (α) and chromium nitride (Cr_2N) phases, and (ii) re-austenitizing the decomposed steel in the temperature range of 1080-1250 °C followed by water quenching.

In order to inhibit formation of sigma and chi phases the 740-1000 °C temperature range seems to be a proper heat treatment window for isothermal decomposition of austenite via the $\gamma \rightarrow \alpha + \text{Cr}_2\text{N}$ eutectoid transformation. As the precipitation of the Cr_2N requires diffusion of the Cr and N atoms the expected TTT diagram should have C-type form. The nitrogen redistribution is needed to impoverishment of the austenite in nitrogen which makes it unstable. On the lack of empirical TTT diagram and also difficulties in theoretical calculation of such diagram, to achieve the optimum heat treatment conditions for decomposition of the nitrogen-saturated austenite, the SN-12H steel samples were isothermally heat treated at 550 °C, 700 °C and 900 °C for various times of 5 min, 10 min, 15 min, 1 h, 2 h and 4 h. The advancement of the nitrogenous eutectoid transformation was investigated from the cross sectional metallographic microstructures. Based on the many microstructural observations it was found that, the nose of the TTT diagram is placed around the 900 °C where the austenite is fully decomposed in a short time. The employed

time/temperature-sequence diagram for grain refinement of the SN-12H steel samples in this paper is presented in Fig. 5.

3.3. Decomposition of as solution nitrided (austenitic) steel

Fig. 6 shows microstructure of the SN-12H steel sample after isothermal heat treatment at 700 °C for 4 h. The decomposed structure appeared as white or dark regions, as indicated with A and B letters in Fig. 6a, respectively. The high magnification SEM images of these regions show that, in both areas austenite decomposes into ferrite and chromium nitride precipitates. However, there are lower amounts of chromium nitride precipitates in white areas than the dark ones (Fig. 6b and c). The EDS analysis of these areas (Table 2) shows that the dark areas are richer in nitrogen than the white areas.

3.4. Re-austenitizing of decomposed steel

To obtain fine grained austenitic structure, the samples with decomposed structure (α +Cr₂N) were subjected to re-austenitizing treatment. Fig. 7 represents optical micrographs of corners and core parts of the decomposed steel plate after re-austenitizing treatment at 1200 °C for 0.5 h followed by water quenching.

It is observed that upon re-austenitizing, the transformation of ferrite into austenite takes place (Fig. 7a, b and c) throughout the sample thickness. Areas of the newly formed austenite are appeared as white areas in Fig. 7. Optical micrograph of the central part of the sample shows that transformation to the austenite starts in many nucleation sites inside the initial structure (Fig. 7b). Impingement of a great number of growing austenite crystals leads to formation of a relatively fine-grained structure. However, existence of bi-phase (ferrite + austenite) regions in center part of the sample, as indicated by arrow in Fig. 7b show an incomplete transformation of ferrite to austenite.

In addition, high magnification micrographs of sample corners (Fig. 7a and c) reveal that some of the chromium nitride precipitates present in the form of spheroidized or lamellar particles (the small dark spots/bands in the white areas) within the newly formed austenite. Therefore, it seems that two processes take place at the same time: the formation of austenite grains from ferrite and the dissolution of chromium nitrides in the austenite lattice.

As the re-austenitizing time increases to 1 h (Fig. 8) all the ferrite transforms into austenite (Fig. 8b) and the chromium nitrides dissolves within the newly formed austenite, becoming thinner and thinner. However, small particles of chromium nitrides still remain within the austenite grains in the corner part of the sample (Fig. 8a and c). This means that ferrite-to-austenite transformation ends before the complete dissolution of the chromium nitride precipitates.

Therefore, full dissolution of the chromium nitride precipitates requires longer holding times at 1200 °C. In this case, the newly formed austenite grains will coarsen due to high temperature exposure during re-austenitizing.

3.5. Decomposition of homogenized austenitic steel

According to Fig. 6 and Table 2 one can conclude that the addition of nitrogen into steel by gas absorption at solid state induces non-uniform distribution of nitrogen. This non-uniformity originates itself from the fact that: i) the nitrogen concentration is maximum on the outward surface and at the sample corners and decreases toward the sample core, ii) nitrogen diffusion as well as nitrogen concentration during nitriding process depends on the grains orientation (firstly the initial ferrite and subsequently the resulted austenite).

It seems that to obtain a grain refined, precipitate-free microstructure the nitrogen concentration over the entire cross section of the full austenitized (SN-12H) sample should be homogeneous. Such homogenization involves diffusion of nitrogen. However, the applied homogenization process requires special conditions. For example homogenization under pure argon atmosphere results in nitrogen loss from the sample surface. Moreover, prolonged exposure times under nitrogen gas pressure of 0.25 MPa results in Cr₂N precipitation [25]. Therefore, in this study the SN-12H samples were homogenized at 1200°C for 10 h under nitrogen gas pressure of 0.1 MPa to prevent nitrogen loss and chromium nitride precipitation before being subjected to grain refinement process. Typical optical micrograph of the SN-12H sample after homogenizing heat treatment (SN-12H-H) is shown in Fig. 9. The microstructure of SN-12H-H sample is composed of equiaxed austenite grains with the average grain size of 100 μm.

Fig. 10 represents SEM images of microstructure of SN-12H-H sample after isothermal heat treatment at 700 °C for 1 and 4 h. The chromium nitride precipitates are nucleated predominately at the grain boundaries and around inclusions in the form of colonies. Formation of eutectoid structure proceeds subsequently by growth of these colonies into the austenite grains (Fig. 10a). After isothermal heat treatment for 4 h at 700 °C, the SN-12H-H sample is fully transformed to eutectoid structure (Fig. 10b). The resultant eutectoid structure is similar to that of pearlitic structure in plain-carbon steels and can be termed as nitrogenous pearlite. On the other hand, comparing figures 10b and 6, indicates that the decomposed structure is more uniform in the SN-12H-H sample than the SN-12H sample.

Fig. 11 indicates SEM image showing morphology of Cr₂N precipitates in the eutectoid structure. For revealing the precipitate morphology the polished surface has been deep-etched with 50% HCl+25% HNO₃+25% H₂O (vol. %). From the micrograph it appears that Cr₂N has strip-like morphology.

3.6. Microstructure of grain refined steel

Fig. 12 represents an optical micrograph of the grain refined steel. By re-austenitizing the SN-12H-H sample with a decomposed (α +Cr₂N) structure at 1200 °C for 10 minutes followed by water quenching, fine grained austenitic structure with an average size of 20 μ m was obtained. Comparing figures 12 and 8 implies the substantial influence of intermediate homogenization treatment on reduction of the re-austenitizing time.

Therefore, for grain refinement of nickel and manganese free austenitic steels fabricated by solution nitriding, to ensure the microstructural uniformity, the nitrogen must be uniformly distributed over the entire cross-section. The microstructure non-uniformity induced during pressurized solution nitriding, can be reduced by homogenizing heat treatment under controlled atmosphere.

3.7. Micro-hardness of the grain refined steel

Fig. 13 displays Vickers micro-hardness of the base material (nitrogen free ferritic steel) and the as-solution-nitrided steel after homogenizing heat treatment (SN-12H-H sample) and grain refinement (SN-12H-R sample). Hardness of the SN-12H-H sample is significantly higher than that of the steel without nitrogen and conventional AISI 316L steel. In addition, micro-hardness test results revealed that the hardness is increased from 270 HV_{0.5} to 347 HV_{0.5} by decreasing the grain size from 100 μ m to 20 μ m as expected according to the Hall-Petch relationship.

3.8. Comparing austenite decomposition in Ni- and Mn- free and Ni-free austenitic steels

Conventional Ni-free HNASSs for biomedical applications generally contain more than 12 Wt. % manganese [6]. The phase diagram of these steels exhibits that by slow cooling or isothermal heating, austenite does not transform to ferrite and the austenitic matrix remains stable until ambient temperature. Although that, the Cr₂N precipitation may occur [27]. At prolonged ageing times formation of sigma and chi phases also was reported [28]. The Cr₂N precipitation behavior during austenite decomposition in the investigated Ni- and Mn-free HNASS is quite different with Ni-free HNASSs for the following reasons:

i) In the conventional Ni-free HNASSs, during the isothermal heat treatment, supersaturated austenite becomes unstable and decomposes to nitrogen-depleted austenite and Cr₂N. However, in the investigated Ni- and Mn-free HNASS, according to the calculated phase diagram and also the obtained experimental results the austenite phase decomposes to ferrite and Cr₂N during isothermal heat treatment below 1000 °C.

ii) In the Ni-free HNASSs nucleation and growth of the Cr_2N take place through a discontinuous or cellular precipitation (i. e. $\gamma_{\text{supersaturated}} \rightarrow \gamma_{\text{saturated}} + \text{Cr}_2\text{N}$). Discontinuous precipitation of Cr_2N precipitation during aging of Ni-free HNASSs has been extensively studied in the literature for example by Rovatti et al. [29] in Fe-20Cr-17Mn-2.5Mo-0.2C-0.8N steel at 800 and 850 °C, by Vanderschaeve et al. [30] in Fe-18Cr-19Mn-2.5Mo-0.12V-0.9N steel between 700°C and 900 °C and by Feng et al. [31] in Fe-18Cr-12Mn-0.48N steel from 700 °C to 950 °C. However, in Ni- and Mn-free HNASS, the precipitation of Cr_2N proceeds via diffusion of the chromium and nitrogen by eutectoid transformation (i.e. $\gamma \rightarrow \alpha + \text{Cr}_2\text{N}$).

iii) The precipitation of Cr_2N in the Ni-free HNASSs during thermal processes such as; aging, hot forging and welding, leads to the significant deterioration of mechanical properties and corrosion resistance. Therefore, most of the recent studies focused on the thermal stability of Ni-free HNASSs. It has been reported by Knutsen et al. [32] that micro-alloying with small addition of vanadium and niobium form stable nitrides and reduces nitrogen available for forming Cr_2N precipitates. In the Ni- and Mn-free HNASS, unlike the Ni-free HNASS, the $\gamma \rightarrow \alpha + \text{Cr}_2\text{N}$ eutectoid transformation could be effectively used for grain refinement. The successful grain refinement requires that the $\gamma \rightarrow \alpha + \text{Cr}_2\text{N}$ phase transformation and the re-austenitizing occur uniformly. This, in turn, demands a homogenization heat treatment before grain refinement.

4. Conclusions

In this study grain refinement of the nickel and manganese free Fe-22.75Cr-2.42Mo-1.17N high nitrogen austenitic stainless steel plates produced by pressurized solution nitriding in the solid state was studied by applying a two-stage isothermal heat treatment procedure. To achieve successful grain refinement a homogenization heat treatment before grain refinement was applied. Based on the obtained results, the following conclusions can be derived:

- 1- Fe-22.75Cr-2.42Mo-1.17N alloy undergoes eutectoid transformation, $\gamma \rightarrow \alpha + \text{Cr}_2\text{N}$, during isothermal heat treatment below 1000°C. The chromium nitride precipitates nucleate mostly from grain boundaries dispersed in the ferritic matrix forming eutectoid colonies. The Cr_2N precipitates in the nitrogenous eutectoid structure exhibit strip like morphology.
- 2- The nitrogenous pearlite in the as-solution-nitrided steel exhibits non-uniform distribution of the Cr_2N precipitates. This could be related to non-uniform distribution of nitrogen.

- 3- The Cr_2N nitrides do not completely dissolve during re-austenitizing at 1200°C for as long as 1 h due to the non-uniform distribution of nitrogen in the as-solution-nitrided steel plate.
- 4- A uniform eutectoid structure was obtained after homogenization heat treatment at 1200°C for 10 h.
- 5- By homogenizing of nitrogen in the entire cross section and grain refinement heat treatment, the grain size of nickel and manganese free austenite was successfully refined to $20\ \mu\text{m}$. Grain refined nickel and manganese free high nitrogen austenitic stainless steel exhibited a hardness value of $347\ \text{HV}_{0.5}$.

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Table captions:

Table 1. Chemical composition of Fe-Cr-Mo steel prepared in this investigation (wt.%).

Table 2. Chemical analysis (wt.%) of area A and B indicated in Fig. 6a.

Figure captions:

Fig. 1. Optical micrographs showing cross-sectional microstructure of Fe-22.75Cr-2.42Mo steel before (a) and after (b) solution nitriding.

Fig. 2. X-ray diffractograms of Fe-22.75Cr-2.42Mo steel before (a) and after (b) solution nitriding.

Fig. 3. Average nitrogen content of the nitrogen free (ferritic) and the as-solution-nitrided (austenitic) steels.

Fig. 4. Calculated phase diagram of Fe-22.75Cr-2.42Mo-(0-2)N alloy system, using the Thermocalc software and TCFE6 database.

Fig. 5. Applied time/ temperature sequence diagram for grain refinement of the austenitic steel.

Fig. 6. Optical micrograph of the SN-12H sample after isothermal heat treatment at 700°C for 4 h (a) and SEM images of area A (b) and B (c) according to Fig. 6a.

Fig. 7. Optical micrographs of corner (a, c) and center parts (b) of decomposed SN-12H sample after re-austenitizing at 1200 °C for 0.5 h.

Fig. 8. Optical micrographs of corner (a, c) and center parts (b) of decomposed SN-12H sample after re-austenitizing at 1200 °C for 1 h.

Fig. 9. Optical micrograph showing the cross-sectional microstructure of the SN-12H-H sample.

Fig.10. Typical scanning electron micrographs of SN-12H-H sample after isothermal heat treatment at 700 °C for (a) 1 and (b) 4 h.

Fig. 11. Scanning electron micrograph showing morphology of chromium nitride precipitates in the eutectoid structure.

Fig.12. Optical micrograph showing the cross-sectional microstructure of the grain refined steel.

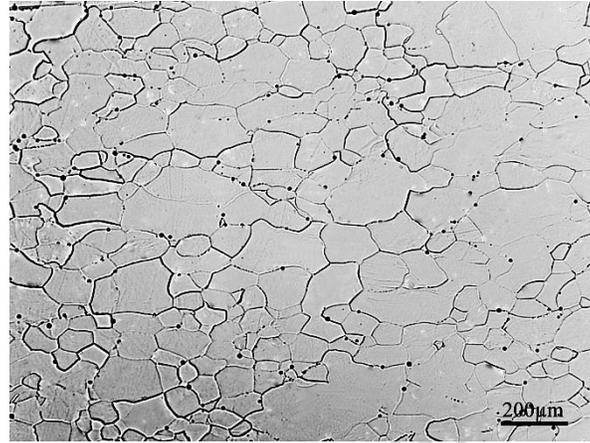
Fig. 13. Vickers micro-hardness of the nitrogen free (ferritic), homogenized (SN-12H-H) and grain refined (SN-12H-R) austenitic stainless steels.

Table 1.

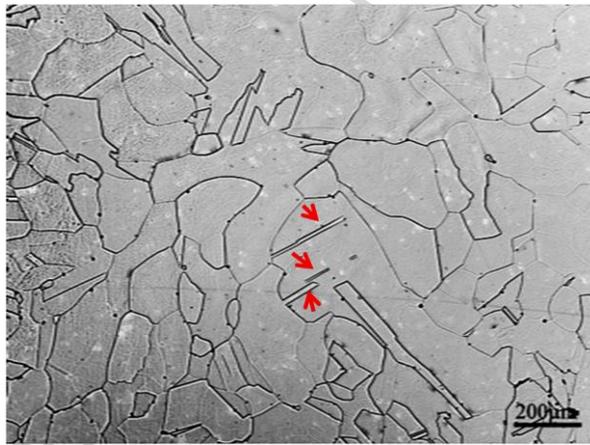
C	Cr	Ni	Mn	Mo	Si
≤0.002	22.753	0.045	0.100	2.420	0.052
Cu	Al	N	P	S	Fe
≤0.50	0.05	0.030	0.010	0.007	balance

Table 2.

Area	Fe	Cr	Mo	N
A	75.1	21.9	1.8	1.2
B	70.1	24.2	2.7	3.0

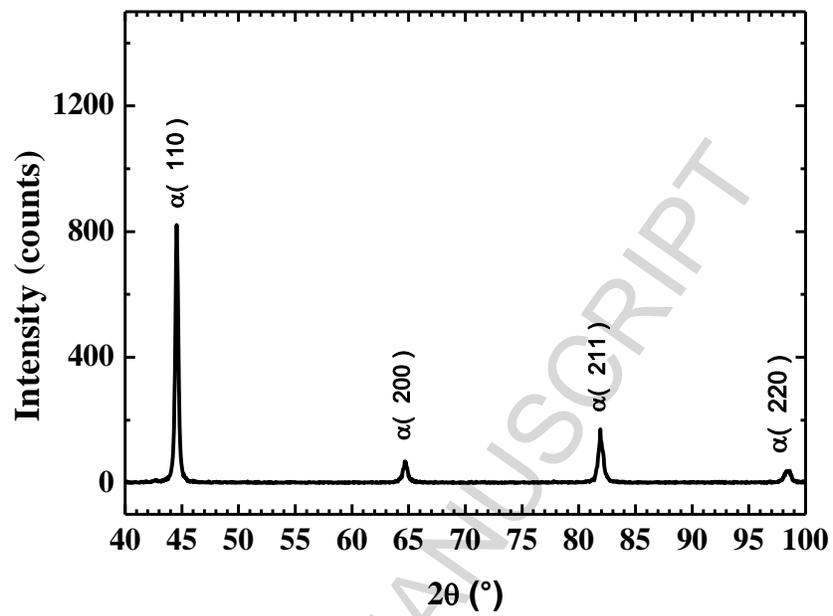


(a)

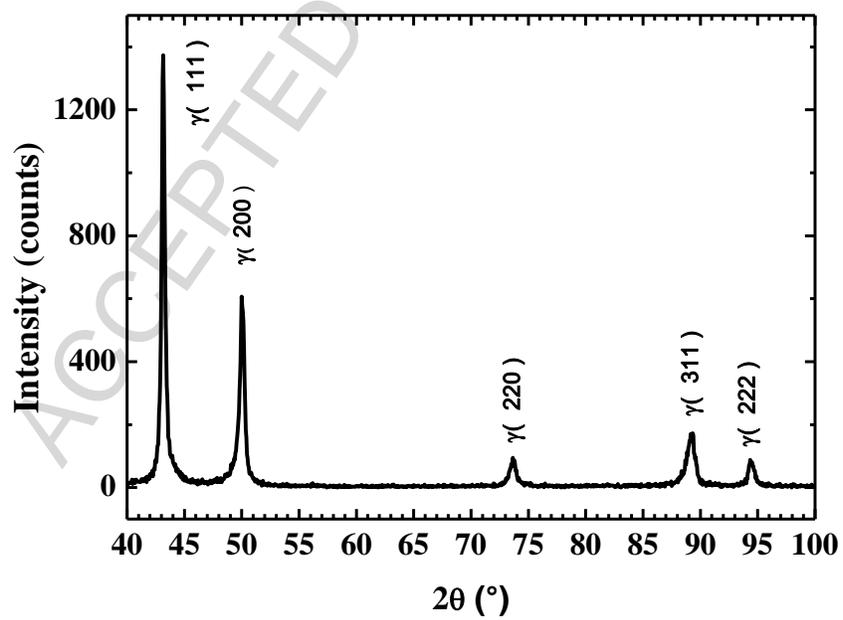


(b)

Fig. 1.



(a)



(b)

Fig. 2.

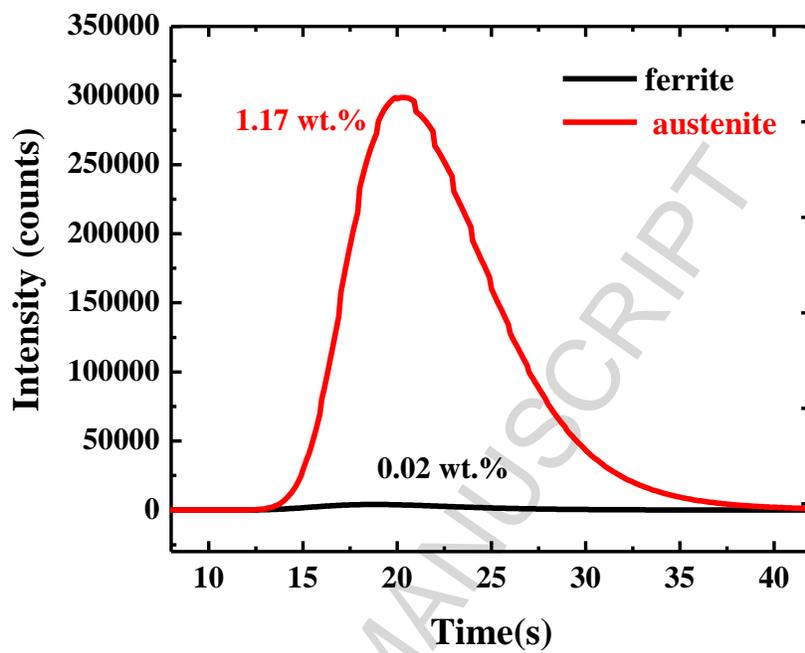


Fig. 3.

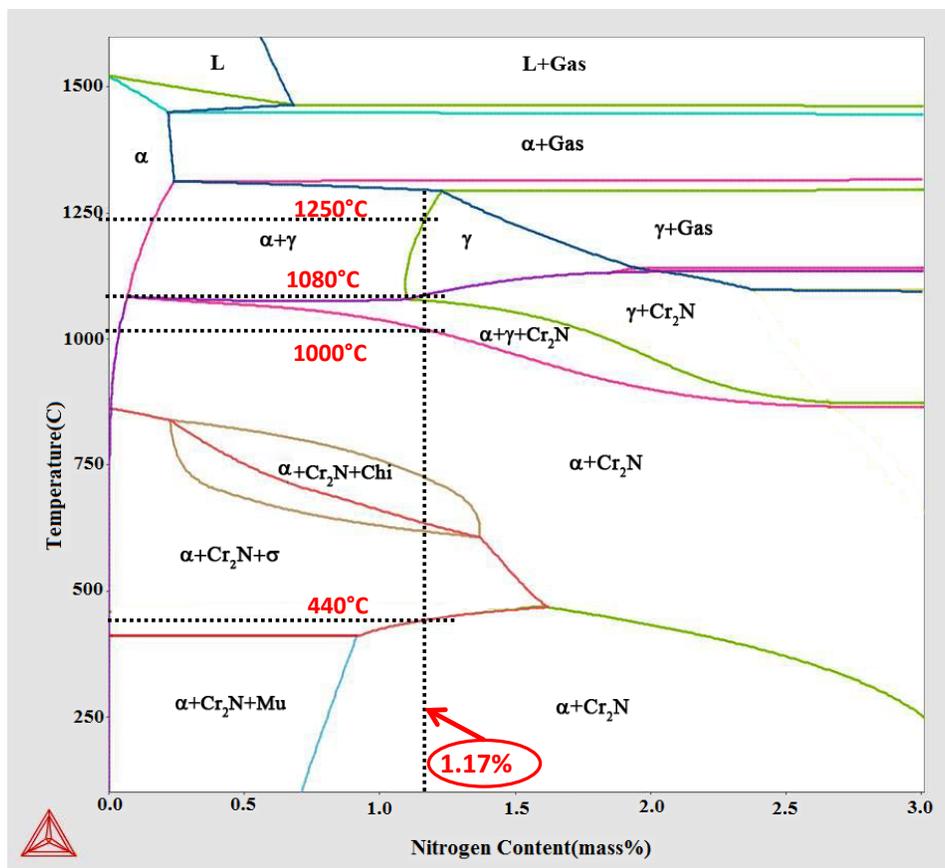


Fig. 4.

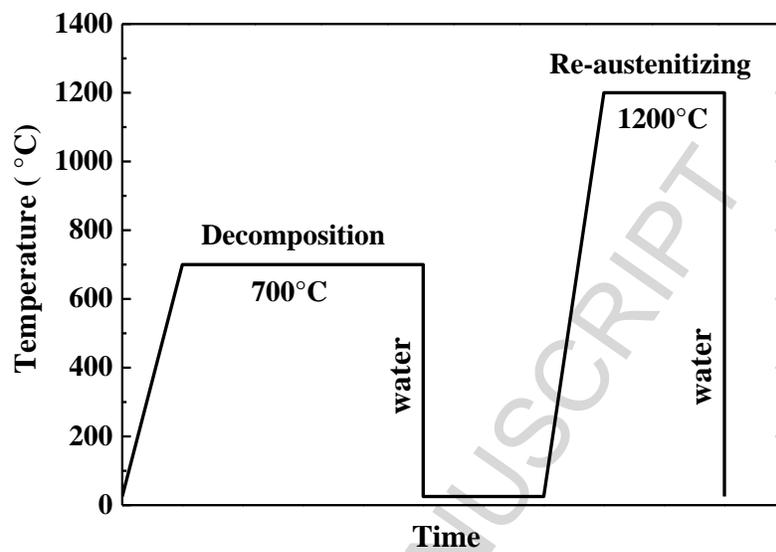
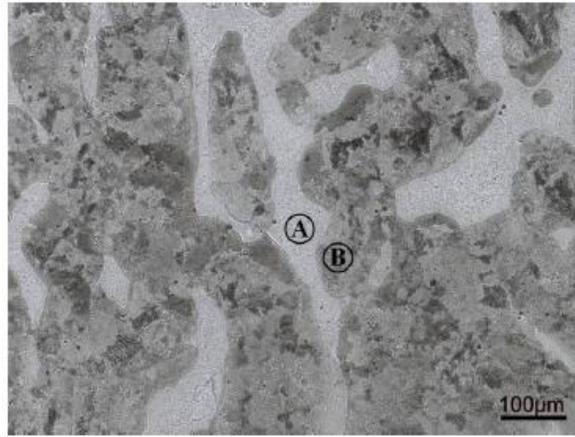
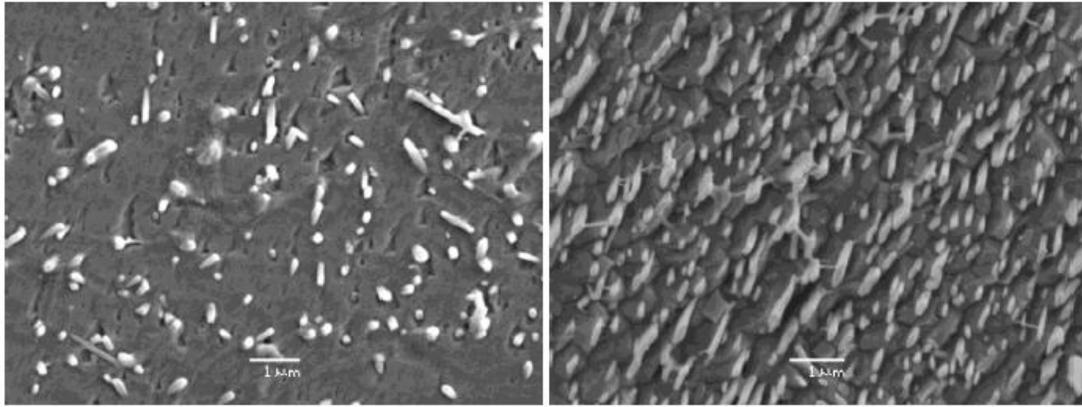


Fig. 5.



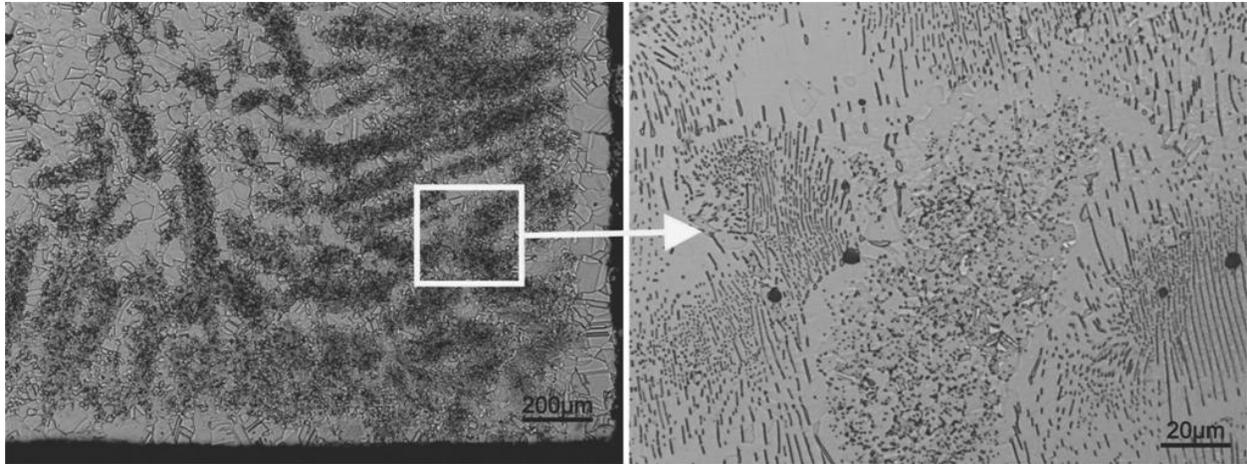
(a)



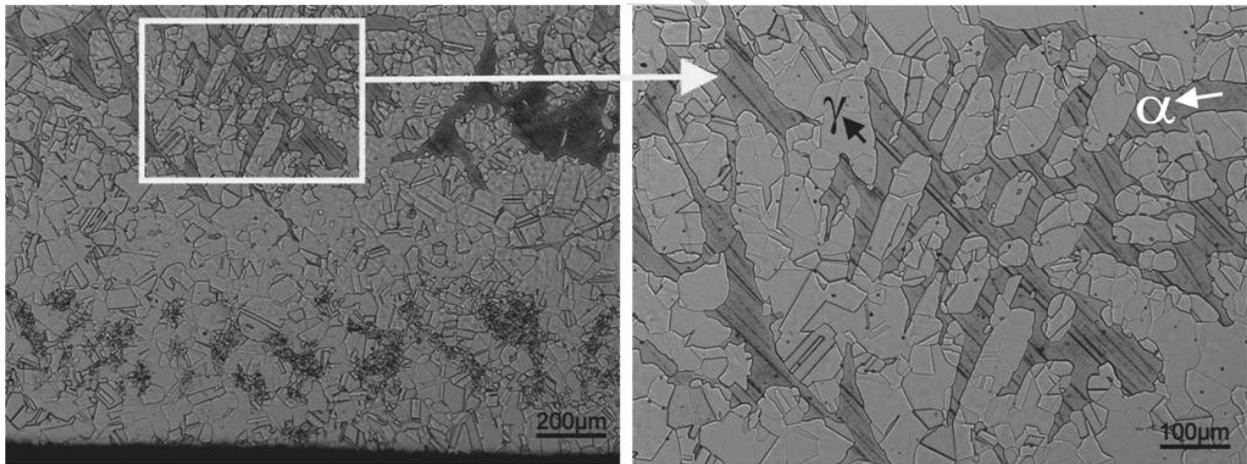
(b)

(c)

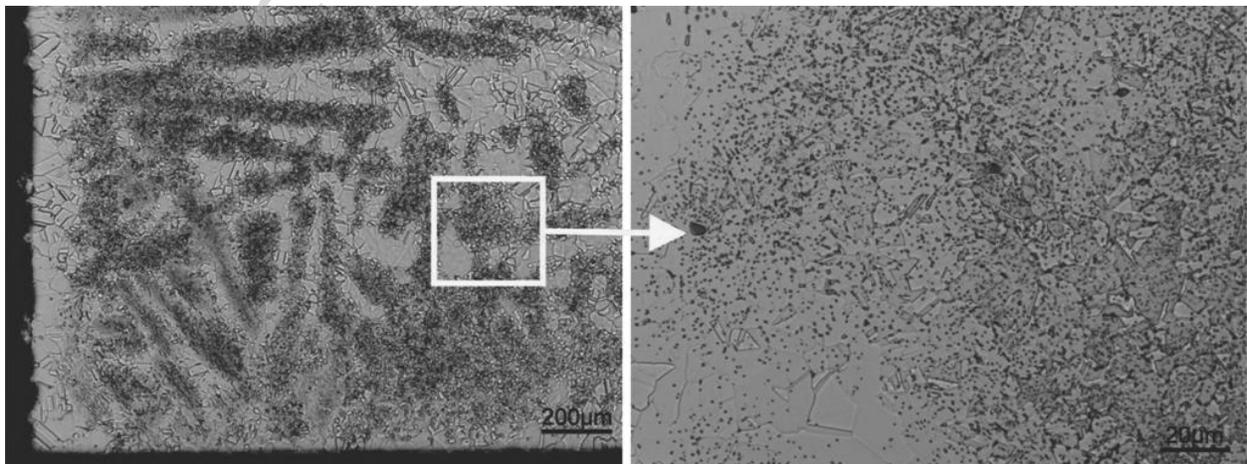
Fig. 6.



(a)

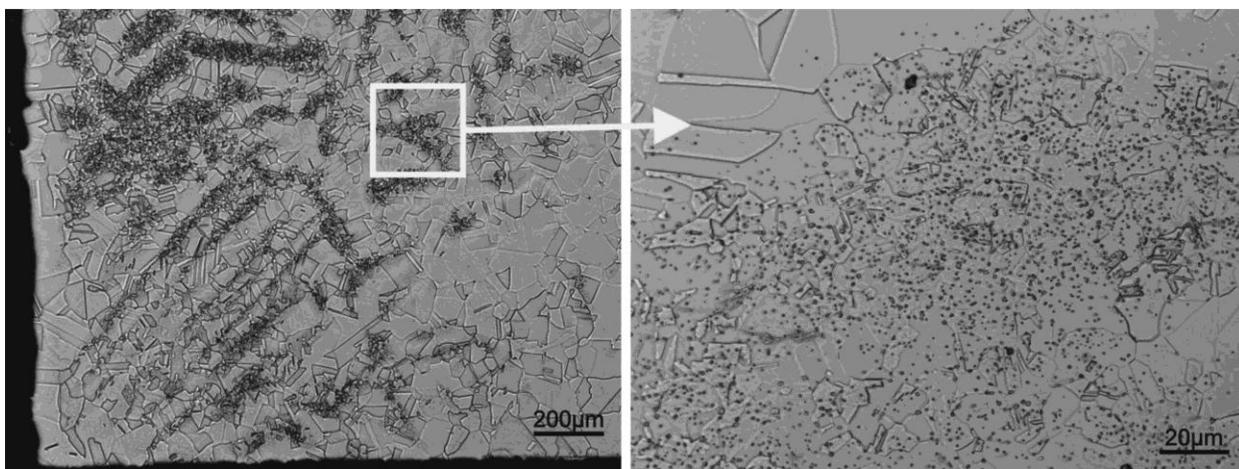


(b)

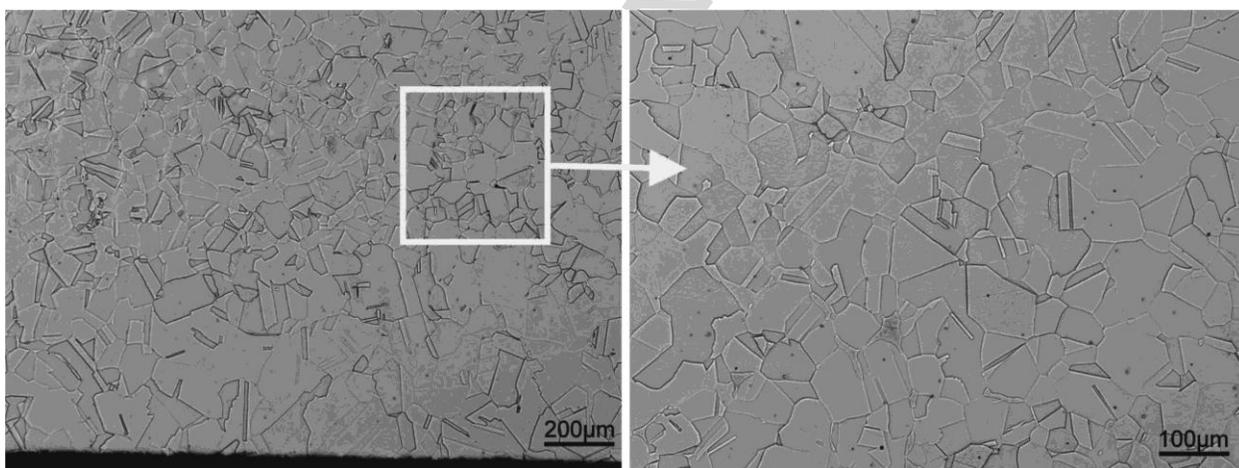


(c)

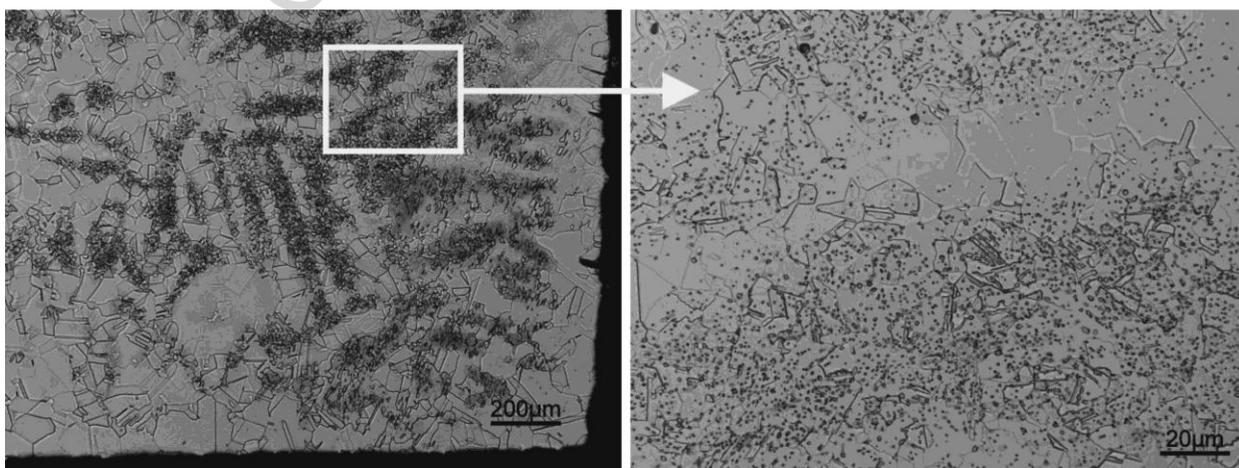
Fig. 7.



(a)



(b)



(c)

Fig. 8.

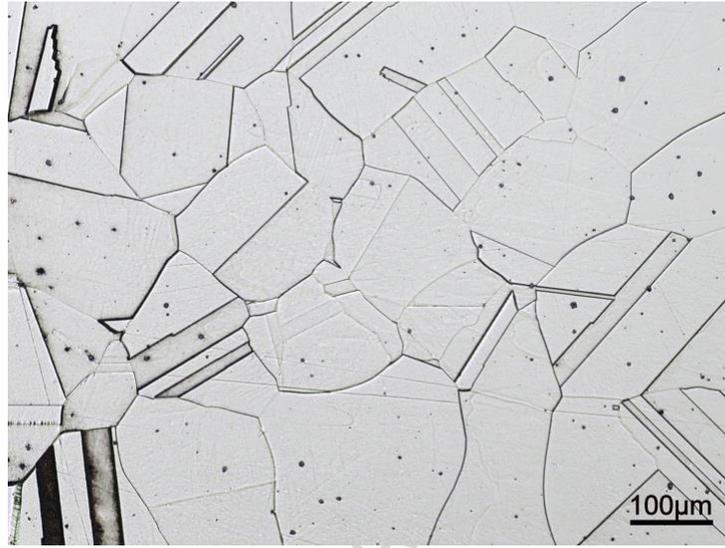


Fig. 9

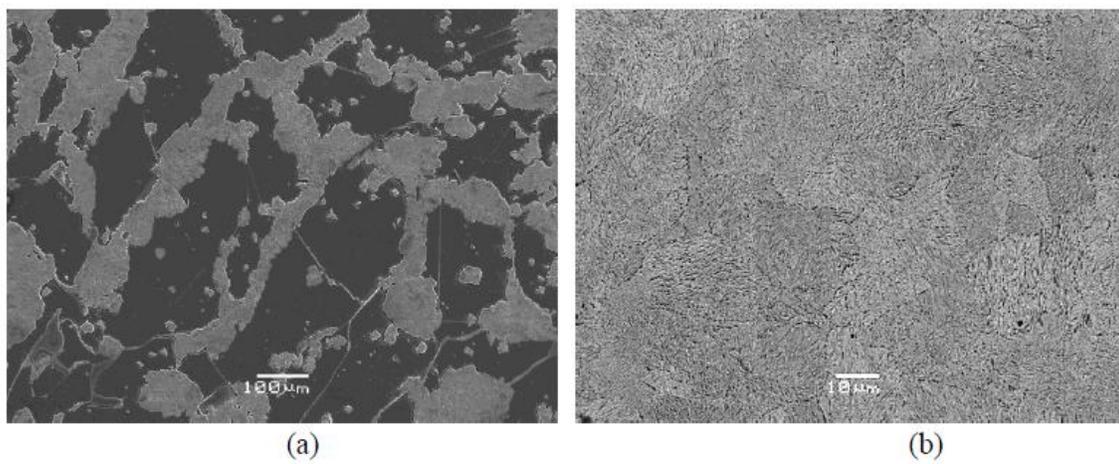


Fig.10.

ACCEPTED MANUSCRIPT

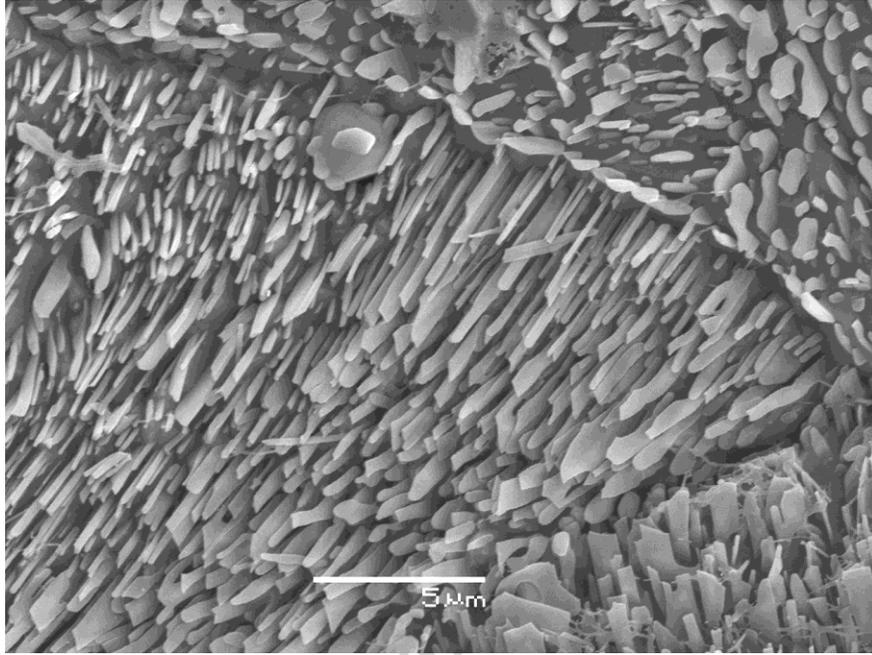


Fig. 11.



Fig.12.

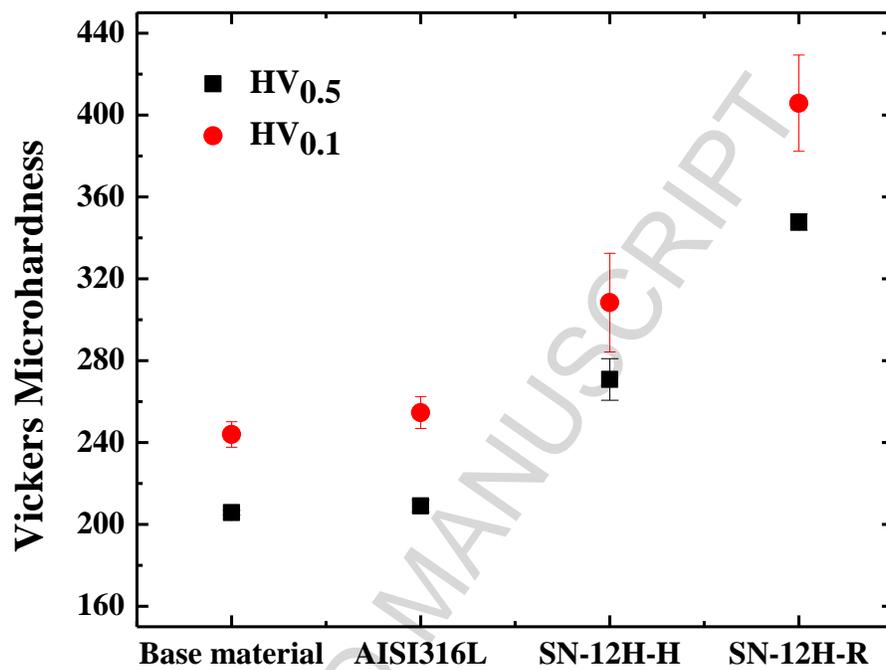


Fig. 13.

Research Highlights

- Successful grain refinement of Fe-22.75Cr-2.42Mo-1.17N steel by heat treatment.
- Using the $\gamma \rightarrow \alpha + \text{Cr}_2\text{N}$ reaction for grain refinement of a Ni and Mn free HNASS.
- Obtaining a single phase austenitic structure with average grain size of $\sim 20 \mu\text{m}$.
- Incomplete dissolution of Cr_2N during re-austenitizing at 1200°C for long times.
- Reducing re-austenitizing time by homogenizing treatment before grain refinement.