# Effect of Low Temperature Aging of Type 316L Austenitic Stainless Weld Metal on Transformation of Ferrite Phase

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The effect of low temperature aging of type 316L austenitic stainless weld metal on the transformation of ferrite phase was studied. Some specimens were aged at temperature 400ºC at various holding times ranging from 100 to 5000 hrs. The ferrite content of the specimens was estimated before and after aging. It can be seen that the ferrite content decreased very slightly with increasing the aging time under low temperature aging when it was measured by Magne Gauge. Microstructure changes before and after aging were noticed. When observing the microstructure change of ferrite content being evaluated by optical metallography, it can be noted that the ferrite phase content reduced to 30% after aging for 500 hrs, while the reduced ferrites phase content reached at 60% after aging for 5000 hrs. Also, the microstructure evolution showed that the ferrite/austenite interface changed from smooth line into corrugated interface like saw-teeth after 5000 hrs aging.

In the present study, the observed contradiction between the appearance of ferrite phase microstructure and the measured ferrite content using a Magne Gauge could be resolved by assuming that the dissolved ferrite content decomposed into α and ά, which kept the magnetic effect as a ferrite phase. It can be concluded that the ferrite number (FN) measurements were not sensitive to the decomposition of ferrite into α and ά, since they were a measure of the amount of presented ferromagnetic phase, and both α and ά were ferromagnetic constituents. These were significantly observed for early stage of aging till 1000 hrs, while at 5000 hrs aging, a slight change of FN could be attributed to G phase precipitate, which was a FCC phase.

## 1. Introduction:

Many nuclear components, such as primary piping of reactors made of austenitic stainless steels due to their excellent mechanical and corrosion properties at high temperature, are particularly containing molybdenum such as AISI 316 stainless steel. Also low carbon stainless steels may be used to reduce the effect of sensitization of the base metal. Some alloying elements such as molybdenum are added to improve the mechanical properties at elevated temperature. The manufacturing processes are mainly achieved by using welding processes, which create weld metal zone and heat affect zone. Austenitic stainless steel weld metal normally has a duplex structure that contains variable amounts of ferrite. This ferrite phase is a metastable phase and forms as a result of rapid solidification rate during the welding process [1].

It is recognized that the sufficient ferrite content as a second phase in the weld effectively prevents the hot cracking. On the other hand, the ferrite phase in austenitic stainless steel weld metals may affect the metallurgical properties and particularly degrade the mechanical properties under service at high temperature. During service, the stainless steel weldments that work at temperatures below 475°C are classified as low temperature aging from a point of view of aging. It is almost important to obtain a detailed knowledge of the precipitated phases responsible for hardening and embrittlement the ferrite of austenitic weld metal and duplex stainless steels, since a given ferrite content can be the basis for establishing the relations between the embrittlement and the chemical composition of the material [2].

The aim of the present work is to study the effect of low temperature aging on the ferrite transformation and microstructure evolution of weld metal type 316L up to 5000 hrs aging at 400°C.

## 2. Experimental Work:

### 2.1. Heat treatment procedure

Austenitic stainless steel weld metal specimens of type 316L were aged at 400ºC at various holding times ranging from 100 to 5000 hrs followed by air-cooling. The heat treatment process was performed in a muffle furnace automatically controlled with accuracy of ±5°C. An additional Ni-Ni Cr thermocouple attached to a digital thermal indicator was used to check the temperatures at the furnace from time to time. The chemical composition of the weld metal is shown in Table (1).

**Table (1):** Chemical composition of electrode 316L

| Element | C | Cr | Ni | Mn | Si | P | S | Mo | Fe |
|---|---|---|---|---|---|---|---|---|---|
| Electrode (wt%) | 0.02 | 18.5 | 12 | 0.8 | 0.7 | _ | _ | 2.6 | Bal. |

### 2.2. Measurement of Ferrite Number (FN)

Ferrite Number was determined using a Magne Gauge Instrument. The instrument was calibrated by US National Bureau of Standards (NBS) according to the American Welding Society (AWS) Standard A4-74. The ferrite contents of specimens were estimated before and after aging. The ferrite numbers were measured as a function of aging time to evaluate the ferrite transformation. Measurements were taken on each sample before and after aging to eliminate any variation at FN in the as-received condition from specimen to specimen. 10 specimens were measured for each condition to get the mean value as well as the standard deviation.

### 2.3. Metallographic Examination

Metallographic examination was made for the weld deposits in the as-received condition and after weld heat treatment. After polishing the austenitic stainless steel, specimens were etched with 10 ml HCl, 1 gm FeCl, and 10 ml $H_2O$ solution for 20 seconds. Specimens were rinsed with alcohol and dried with hot air. The optical microscope was used for microstructure examination.

## 3. Results:

### 3.1. Ferrite Content Variation after Aging

Table (2) shows the ferrite content (FN) variation against the aging time at 400°C. It can be seen that the ferrite content decrease very slightly with increasing the aging time. The ferrite content (FN) after 5000 hrs decrease to 13.098, which is about 2.8 FN from as received condition value.

**Table (2):** The average ferrite content (FN) variation against the aging time and the standard deviation.

| Aging time, (hrs) | Average of FN | Standard Deviation |
|---|---|---|
| As- received | 15.8809 | 1.104422 |
| 500 hrs | 15.05 | 1.121365 |
| 1000 hrs | 15.091 | 1.423089 |
| 2000 hrs | 13.55 | 1.051498 |
| 5000 hrs | 13.098 | 0.699399 |

A slight change in ferrite content is observed after aging for 500 hrs. The decrease is of order 0.8 FN for 500 and 1000 hrs, 2.3 FN and 2.78 FN for 2000 and 5000 hrs, respectively. The measured ferrite content is reduced about 6% and 17% of the as received value due to aging for 500 and 5000 hrs respectively.

## 4. Microstructure Variation:

### 4.1. As-received condition

Figure (1) shows the microstructure of the top surface of the weld metal. The as received condition shows that the microstructure had an austenite (white phase) as a matrix and ferrite as the second phase which appears as a black phase. The ferrite morphology has a vermicular shape i.e.: skeletal morphology. The ferrite content is estimated as 15.9 FN.

### 4.2. After aging

Figures (2-7) show the microstructure variations due to aging for 100, 200, 500, 1000, 2000, 3000, 4000 and 5000 hrs respectively. Compared to the as received condition, the ferrite phase network is affected by aging time. At the early stage of aging, no significant change is occurred till 200 hrs aging as shown in Fig.(2). Increasing the aging time to 500 hrs, the ferrite phase starts to dissolve the secondary arms of ferrite phase as shown in Fig.(3**)**. For further aging till 3000 hrs, the ferrite phase primary arms start to dissolve as shown in Figs.(4-6) for 1000, 2000 and 3000 hrs aging respectively. Also, it can be observed that the ferrite-austenite interface converted from smooth line to corrugated interface like saw-teeth after 5000 hrs aging as shown in Fig.(7).

At increasing the aging time to 4000 and 5000 hrs, the ferrite phase dissolved significantly. However, the ferrite phase content FN shows a slight change in quantity. It is changed from 15.88 at the as received condition to 15.05 after 500 hrs aging. This contradicts to the microstructure of the weld metal which shows a significant reduction on the ferrite phase (black phase). The microstructure changes show that the ferrite phase content reduces to 30% after aging for 500 hrs, and 60% after aging for 5000 hrs. It can be observed that the measure of ferrite phase using Magne Gauge shows different values for aging compared to the values evaluated by using optical metallography.

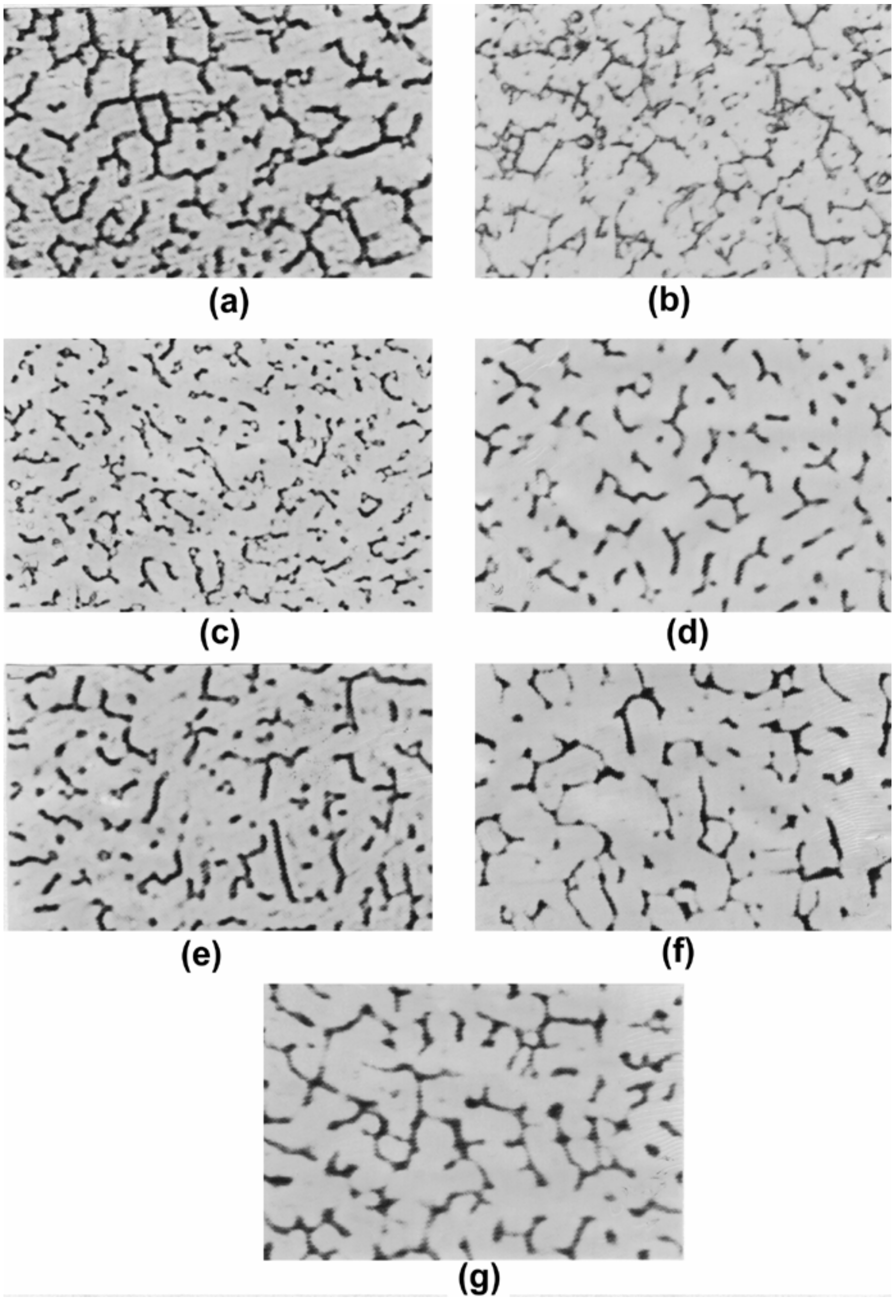

**Fig. (1):** Microstructure evaluation before and after aging X 200, (a) as weld, (b) after 200 hr, (c) 500 hr, (d) 1000 hr, (e) 2000 hr, (f) 3000 hr, Fig(g) 5000 hr.

## 5. Discussion

Since 316L weld metal solidifies as primary delta ferrite dendrites, the cores are highly enriched and depleted in nickel. This causes the primary dendrites of 316L weld metal to have a composition similar to the ferritic stainless alloy, where there is tendency for the presence of precipitate which might be found after aging.

### 5.1. Ferrite Content Changes

The ferrite in the welds is metastable and results at the incomplete transformation of ferrite to austenite during cooling after welding. Therefore, the ferrite numbers are measured as a function of aging time to evaluate the ferrite stability. However, measurements are taken on each sample before and after aging to eliminate any variation at FN in the as-received condition from specimen to specimen. The result of measuring ferrite content in the as-weld condition was discussed elsewhere [1].

In the investigation of the low temperature aging behaviour of type 308 stainless steel weld metal, J. M. Vitek et al. [2] found that results showed no change in ferrite content which was found at aging treatments up to 10,000 hrs at 475 °C. Also, Hale et al. [3] showed that no change in FN after aging type 308L stainless steel welds at 375 and 400 °C was observed. However, J. M. Vitek et al. [2] found that after aging to 20000 hrs, a drop in FN to 3 was indicated that some significant loss in ferrite content took place after such extensive aging. They commented that the FN measurements are not sensitive to decomposition of ferrite into α and ά since they are a measure of the amount of presented ferromagnetic phases. It can be concluded that the ferrite decomposition could be hard to estimate exactly by using the magnetic measurement at early stage of aging. However, the ferrite content has a significant transformation after 5000 hrs aging.

### 5.2. Microstructure Evolution

**As-received**: Stainless welds can be classified into three microstructure types, A, B and C, according to their general microstructure and the morphology of ferrite [4-5]**.** This results that ferrite phase is a metastable phase at room temperature. In the welds of type A the delta ferrite, if any, is located at cell boundaries and has a vermicular morphology, while in type B it is mainly located to the axes of the cells or dendrites and not between them, its morphology being either vermicular or lathy. In welds of type C, it is the lathy morphology that is dominant. In the present study the ferrite phase is primary solidified according to the ratio of the chromium to nickel equivalent $Cr_{eq} \backslash Ni_{eq}$

= 1.72 which is greater than $Cr_{eq} \setminus Ni_{eq}$ = 1.35. According to this ratio, the main morphology of the studied weld deposit could be classified as type A.

The aging behaviour of welded type 308 stainless steel, which was evaluated by mechanical property testing and microstructure examination, was studied [6]. Aging was carried out at 470°C for up to 20,000 hrs. The initial material consisted of austenite with approximately 10% ferrite. They showed that the ferrite in welds was subjected to spinodal decomposition during low temperature aging at 475°C. G-phase formation on dislocations in ferrite was also found. Microstructure analysis by H. G. Ghung et al. [7] indicated that the ferrite decomposed spinodally into iron rich α and chromium-enriched ά. In addition, abundant precipitation of nickel and silicon-rich G-phase was found within the ferrite and $M_{23}C_6$ carbide formed along the austenite ferrite interface.

These effects are similar to the aging behaviour of cast stainless steels occasionally, large G-phase at precipitates were also found along the austenite-ferrite interface after aging more than 1000 hrs [7-8]. The microstructures were evaluated as a function of aging time by means of TEM. Aging resulted in the decomposition of ferrite as well as precipitate formation. A series of micrographs revealing the structural changes as a function of aging time are as follows [2-6]. Short-term aging (≤500 hrs) resulted in the decomposition of ferrite into α and ά. This decomposition was revealed in the form of a mottled appearance of the ferrite. After 2 hrs aging, this mottled structure was not readily observable by TEM but it was clearly seen after 100 and 500 hrs. The mottled appearance is typical to the microstructure found after spinodal decomposition. With longer aging times, areas were often found along the ferrite austenite interface that seemed to be extensions of the ferrite phase. These areas are marked a dark field microscopy using ferrite reflections illuminated these areas. Also, they had the same structure and orientation as the ferrite. The EDS analysis showed that these areas were very rich in iron. The composition of this phase in wt% was: 88 Fe, 8 Cr, 3 Ni and 1 Mn. This composition agrees quietly with that expected for the iron-rich phase determined from the phase diagram for the Fe-Cr system [9]. Therefore, based on the composition and diffraction evidence, this phase concluded to be iron-rich. For aging times of 500 hrs or more, precipitation of this phase within the ferrite was detected.

Two sizes of precipitates were found within the ferrite. Large precipitates (~30 to 50 nm) were found along dislocations within the ferrite. While small precipitates (~5 to 10 nm) were found to be more uniformly distributed within the ferrite. Dark field microscopy indicated that both precipitates had the same structure. Microstructure analysis showed that these precipitates were G-phase, having a cube-on-cube orientation relationship with the ferrite. The lattice parameter of the G-phase was ≈1.13 nm, although in-foil EDS analysis of the precipitates within the ferrite was impossible due to their fine size and interference from the ferrite matrix, qualitative analysis showed that these precipitates were rich in nickel, manganese, and silicon. On occasion, large G-phase precipitates were also found along the ferrite-austenite interface. In addition to the limited number of carbides that formed during thermal cycling of early weld passes, chromium-rich $M_{23}$ $C_6$ carbides were also found to form upon aging. This carbide formed along the austenite-ferrite interface and had a cube-on-cube orientation relationship with the austenite. Extensive carbide formation along the austenite-ferrite interface was also found in agreement to the comparable aging studies on cast stainless steels. The differences in scale amount and morphology of the ferrite as well as compositional variations between cast and welded materials are only of secondary importance.

Chung and Chopra [10] summarized their microstructure results on low temperature aging behaviour of cast stainless steels in the form of a TTT diagram. Their diagram indicated that the spinodal reaction occurred only below ≈425°C. While the results of J. M. Vitek et al [2, 6] studies indicated that the upper limit of the spinodal decomposition reaction in type 308 welds was higher and lied above 475°C. This temperature was composition dependent, but the applicability of kinetic-data based on cast steels to welds, and the fact that Trautwein and Gysel [11] found the same type of embrittlement for cast material aged at temperatures up to at least 450°C implied that Chung and Chopra's upper temperature limit might be too low .

Microstructure studies of aged stainless steel casting materials [12] (CF-8 and CF- 8M) which had about 15-20 % of ferrite phase in austenitic matrix indicated the existence of a FCC phase with a lattice parameter close to 1.1 nm, homogeneously dispersed on the ferrite. This FCC precipitate was tentatively identified as a G phase and its chemical composition was determined by atom probe analysis as being approximately (in atom %) 28 % Si, 24 % Ni, 21 % Fe, 13 % Mo, 12 % Cr, 1 % C. Moreover, Cr profiles determined by the atom probe supported the hypothesis of ά precipitate between the G phase particles. However, ά could not be identified and analyzed at the lower aging temperatures (i.e. ≤ 400°C), which was of interest for nuclear piping.

M. Vrinat *et al*. [8] studied the precipitated phases in the ferrite of aging cast duplex stainless steels that gave the first results of the microstructure study of aged cast products, the chemical compositions and ferrite contents which can be considered as typical for Pressurized Nuclear Power Reactor (PWR) primary piping components. They studied the microstructure which was undertaken on two cast products (cast duplex stainless steels of the CF-8 and CF-8M types) for the evolution. They concluded that by means of transmission electron microscopy on thin foils and on extraction replicas, two precipitated phases were identified in the ferrite of aged cast duplex stainless steels of the CF-8 and CF-8M types. These phases were respectively fcc with a lattice parameter of 1.12 nm (probably G phase) and bcc with a lattice parameter of 0.289 nm (ά). The precipitated phases were analyzed by X-ray Energy Dispersive Spectrometry (EDS) on extraction replicas. S. S. Brenner et al. [13] studied spinodal decomposition of iron–32 at. % chromium at 470°C and found that ferritic stainless steels with more than 13 % Cr were severely embrittled when heated in the temperature range between 400 and 550°C. Also their results of a field-ion microscopy and atom-probe (AP) microanalytical study showed that the ά precipitate morphology in the Fe-32 at. % Cr alloy aged at 470°C was unusual for a metallic system. The microstructure consisted of vein-like, irregularly shaped regions with an average thickness of only 2.0 to 3.0 nm. They found no evidence for crystallographic alignment of the ά regions as it had been previously suggested for a Fe-45X Cr alloy. The structure appeared to be highly interconnected, at least during the early stages of decomposition. It was most likely that this transformation product stemmed from a spinodal reaction occurring within the miscibility gap had been suggested [8] previously. The development of the concentration profiles during aging was consistent to the notion of a continuous transformation mechanism wherein the two-phase microstructure evolved via the progressive amplification of fluctuations towards the equilibrium compositions. Furthermore, the isotropic nature of the morphology resembling phase separation in glasses was not unexpected because of the small strains developed between the Cr-rich and Fe-rich regions. S. S. Brenner et al. [13] also found that coarsening of the isotropic phase mixture occurred early in the precipitation reaction but at a very slow rate. The persistence of the irregular morphology even to aging times ranging upwards to 11,000 hrs was suggested that the interfacial energy between the conjugate phases α and ά was rather low.

Recently, Field Emission Gun Transmission Electron Microscopy (FEG-TEM) was used to investigate the detailed nanoscaled structure in the aged specimens of duplex stainless steel [12]. For the austenite-ferrite phase interface of the specimens aged at 475°C for 2 hrs, it was noticed that there was a sudden change from the modulated contrast in ferrite to an even contrast in the austenite phase. The mottled image of ferrite can be seen more clearly when the electron beam was aligned along the <001> zone axis. The mottled image, which had the appearance of an orange peel, was found in TEM bright field micrographs of aged ferritic and duplex stainless steels. The mottled aspect had been attributed to the nucleation and growth of Cr-rich ά particles or to a spinodal decomposition reaction. Atom probe field ion microscopy had revealed the phase separation due to the spinodal decomposition into an ultra-fine mixture of a Cr-enriched ά and a Fe-rich. In their investigation [14], a periodically modulated contrast occurred in the ferrite without a denuded zone in the immediate vicinity of the austenite/ferrite interfaces. The evidence strongly suggested that the phenomenon of spinodal decomposition occurred in ferrite phase during aging at 475°C. The morphology of the modulated microstructure for the specimens aged at 475°C was given. These micro-graphs revealed phase separation in the specimens aged for 2~64 hrs, but it was difficult to resolve in specimens aged for less than 2 hrs. The scale of this two-phase modulated microstructure was measured to be 1.7, 2.5, 3.3, 4.2, 4.3 and 5.0 nm for aging times of 2, 4, 8, 16, 32 and 64 hrs, respectively. The modulated microstructure was observed to coarsen with aging time, the morphology was being similar. The sequences of FEG-TEM revealed that the two-phase mixture was irregularly shaped and fully interconnected as resembling a sponge, indicative of the typical nature of the isotropic spinodal structure. Nanometer-scaled chemical analysis has been conducted using a FEG-TEM containing an EDS; the data for the specimen aged at 475°C for 64 hrs was illustrated. The fine scale isotropic spinodal decomposition of ferrite phase brought about Cr-rich bright image domains and Fe-rich dark image domains, i.e. ά and α phase separately. It also showed that Mo and Mn were partitioning to the ά phase, while Ni was partitioning to α phase.

In the present study, the contradiction observed between the appearance of ferrite phase microstructure and the measured ferrite content using a Magne Gauge could be resolved by assuming that the dissolved ferrite content is transformed into other phase which have the same magnetic effect i.e. magnetic phase.

From the above discussion, it can be found that the results of the study indicate that the micro-structural behaviour of 316L weld metal aged at 400˚C is quite similar to that found for stainless steel castings CF-8 and CF-8M materials and as well as 308 weld metal that the effect of aging on microstructure and ferrite content are also comparable. Just as in the cast steels, the ferrite are assumed to decompose into a spinodal mechanism and the G-phase is found to precipitate in the ferrite phase.

At low temperature aging, some ferrite phase may be dissolved into rich iron phase (α) and rich chromium phase (ά). Both of these phases have magnetic properties, which are similar to the original ferrite phase. This could be the reason that the measured FN after aging has high magnetic attraction force as if the ferrite has no significant transformation. The slight change in the ferrite content could be attributed to non-magnetic transformed products from the ferrite phase. These non-magnetic phases such as G-phase and $M_{23}$ $C_6$ could be formed. However the studied weld deposit alloy has low carbon content (0.02). So, the possibility of forming carbides is very low, less than (0.003). Therefore the main reduction in the FN could be attributed to the G-phase formation for ferrite phase measured by Magne Gauge. It could be concluded that the ferrite transformation in type 316 L weld metal may be higher than that reseeded by 308. In the present study, the contradiction observed between the appearance of ferrite phase microstructure and the measured ferrite content using a Magne Gauge could be resolved by assuming that the dissolved ferrite content is decomposed into α and ά which keep the magnetic effect as ferrite phase.

## 6. Conclusions:

The measurements of ferrite with Magne Gauge compared to the microstructure variation due to low temperature aging at 400°C till 5000 hrs, led to the following conclusions:

1- The FN measurements are not sensitive to decomposition of ferrite into α and ά since they are a measure of the amount of ferromagnetic phases that is present and both α and ά are ferromagnetic constituents.
2- The present results show that the ferrite content decreases with increasing aging times. It can be observed that most secondary dendrite structure arms disappeared. The ferrite phase dissolved at increasing aging. The microstructure evolution shows that ferrite/austenite interface changes from smooth line into corrugated interface like saw- teeth after 5000 hrs aging.
3- The measured ferrite phase using Magne Gauge shows different values after aging compared to the values evaluated by using optical metallography.
4- Non magnetic phases content which is mainly G-phase produced due to ferrite transformation may be estimated to the reduction in ferrite content.

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