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Thermal, magnetic and composition analyses of the reverse transformation of intermetallic sigma phase to ferrite

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Abstract The reverse transformation of the sigma phase to ferrite in a duplex stainless steel upon heating has been studied by using differential thermal analysis (DTA), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM), X-ray diffraction (XRD), quantitative metallography and magnetic susceptibility measurement. It has been demonstrated that the reverse transformation of the sigma phase to ferrite is sensitively affected by the morphology of the sigma phase. However, EDS has shown that the composition of the sigma phase does not significantly affect its reverse transformation behaviour. Magnetic susceptibility measurements and TEM have revealed that untransformed, residual ferrite is present even after prolonged annealing between 873 and 1173 K and hence it does play a role in the sigma-to-ferrite reverse transformation. Quantitative metallography was employed to follow the coarsening of the sigma phase upon annealing and DTA was used to estimate its enthalpies of dissolution. As a potential application, a method for temperature monitoring using duplex stainless steels and DTA is suggested.

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Introduction

Between about 873 and 1173 K, the ferritic phase (α) of ferritic-austenitic duplex stainless steel transforms to intermetallics (mainly the sigma phase σ), secondary austenite (γ_2) and carbide, i.e. $\alpha \rightarrow \sigma + \gamma_2 + M_{23}C_6$. Above 1173 K, the sigma phase undergoes reverse transformation, i.e. it dissolves and ferrite forms again.

The earliest systematic study on the sigma phase dates back to 1927 (refer to the review from Hall and Algie [1]) and research on the sigma phase is still ongoing nowadays [2]. The sigma phase keeps on catching the attention of researchers because it can form in a wide variety of technologically important transition-metal alloys, and so a thorough understanding of it is of paramount importance. A great number of different techniques, ranging from XRD and magnetic measurements through to electron microscopy, have been performed on the sigma phase over the years. However, it seems that few investigations that use differential thermal analysis (DTA) or differential scanning calorimetry (DSC) have been done. In this regard, the present group of authors reported some preliminary findings recently [3]. Also, almost all research done on the sigma phase so far has focused on the ferrite-to-sigma transformation (between 873 and 1173 K), whereas the reverse sigma-to-ferrite transformation (above 1173 K) has received just very scant attention.

In a previous study, the dissolution of the sigma phase and the re-formation of ferrite was partly explained on the basis of the morphology of the sigma phase and the availability of σ/γ boundaries [3]. It has to be noted that although it was suggested (without any supporting evidence) in the previous study that the main constituents of samples of duplex stainless steels in the initial state were just the sigma phase and secondary austenite, residual

ferrite might in fact be present. And if residual ferrite is present, it certainly would influence the sigma-to-ferrite revere transformation, because σ/α boundaries are ready nucleation sites for the re-formation of ferrite (even readier than the σ/γ boundaries suggested in the previous work [3]). Most importantly, it was conjectured (also without concrete supporting evidence) in the previous work that composition of the sigma phase might be a possible controlling factor [3].

The current work was undertaken to clarify the questions that went unanswered in the previous work [3]. The unanswered questions are: (1) whether residual ferrite exists and for how long it persists in samples of duplex stainless steel; and (2) whether composition of the sigma phase is really a possible controlling factor of the sigma-to-ferrite reverse transformation.

The existence of residual ferrite was studied by a.c. magnetic susceptibility measurements, while the effect of composition was analysed by using EDS. Other supporting experiments include DTA, TEM, SEM, quantitative metallography and XRD.

Experimental details

The nominal composition (in wt%) of the self-fabricated duplex stainless steel was 24.8%Cr, 8.0%Ni, 2.0%Mn, 0.16%Mo, 0.18%Si, 0.05%Cu, 0.021%C, 0.012%P and the balance being Fe. The as-received raw material was first subjected to a solution treatment at 1373 K for 1 h, followed by quenching in water. Subsequently, the material was cold-rolled to 56% reduction in thickness to encourage formation of the sigma phase. Then, the samples were subjected to annealing at 973, 1023 and 1073 K for up to 3017 h, followed by quenching in water. Microstructures of the samples were examined by using a Jeol JSM-820 SEM. A Philips CM20 TEM was used for structural characterisation and composition analysis. In addition to TEM, an a.c. magnetic susceptometer (input-amplitude: 1.000 mV and frequency: 606 Hz; output—in mV), fabricated by the Chinese Academy of Sciences, was also used to check if there was untransformed, residual ferromagnetic ferrite in the annealed samples. A BioScan Optimas Image Analyser was used for phase quantification and a Siemens D500 X-ray diffractometer (CuKα) for phase identification. The longest characteristic dimensions of the sigma phase particles were measured with the aid of the Image Analyser. To study the sigma-to-ferrite transformation, a Perkin Elmer UNIX DTA 7 and a Seiko TG/DTA 220 were used for thermal analysis (purge gas: helium). The DTA 7 was used in (differential scanning calorimetry) DSC mode to obtain the enthalpy of dissolution of the sigma phase. The enthalpy of dissolution of the sigma phase was calculated by computing the area under the peak in the thermogram (refer to Fig. 3). To minimise size effect, the size of the samples for thermal analysis was fixed at $2 \times 2 \times 5$ mm^3.

Results

Microstructures of annealed samples (before DTA measurements)

It is well established that after annealing between about 873 and 1173 K, the main constituents of duplex stainless steels are the sigma phase and austenite [1] and XRD analyses of the present work confirmed this statement again. Other minor phases that might be present in the annealed samples were carbides and untransformed, residual ferrite. Amongst the various constituent phases of the annealed samples, only ferrite is ferromagnetic at room temperature and so only it could induce signals in the magnetic susceptometer. Magnetic measurements showed that some ferrite did remain untransformed in all of the samples (Table 2). As annealing proceeded, the a.c. magnetic susceptibility gradually decreased, thereby indicating that the amount of untransformed ferrite diminished gradually in quantity (Table 1). TEM examination revealed that although the amount of untransformed ferrite was not high, it did remain in samples even after prolonged annealing in the temperature range used in this work. For instance, there was untransformed ferrite even in samples that had been annealed at 1073 K for 3000 h (Fig. 1). The selected-area diffraction (SAD) pattern taken from the ferrite phase shown in Fig. 1 pertains to the bcc lattice (inset of Fig. 1). Therefore, the amount of untransformed ferrite was inversely proportional to annealing temperature, inasmuch as ferrite decomposition is faster and more complete as temperature goes up [4]. This is because as the transformation to the sigma phase proceeds, the ferrite will be gradually depleted of alloying elements like Cr and Mo [5–11]. Therefore, the driving force for further transformation to the sigma phase will be lessened and so the transformation from ferrite to the sigma phase slows down significantly. In the study conducted by Vitek et al. [5] on duplex stainless steel weld metals, some of the ferrite remained untransformed for at least up to 10000 h at 973 K.

Table 1 Magnetic susceptibilities of samples annealed at 973 K for different times

Annealing duration (h)	0	168	1000	2980
Specific magnetic susceptibility (mV/g)	9.874	0.884	0.212	0.113

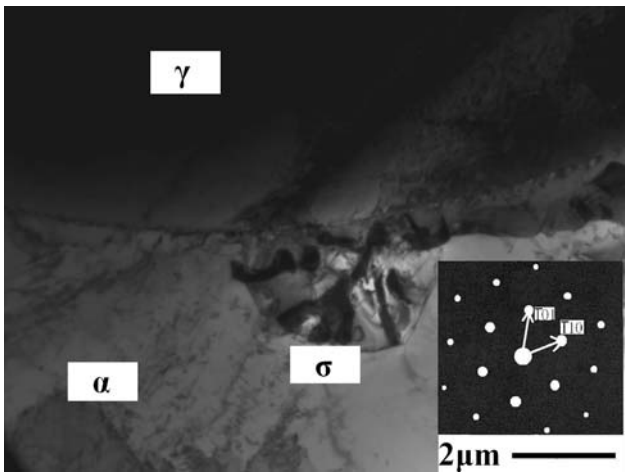

Fig. 1 TEM micrograph showing untransformed ferrite in a sample that had been annealed at 1073 K for 3000 h (inset shows the selected-area diffraction (SAD) pattern of the ferrite phase)

Upon heating during DTA measurements, the existence of residual ferrite provides very ready nucleation sites (σ/α boundaries) for the re-nucleation of ferrite. Therefore, in addition to sigma/austenite boundaries as suggested in the previous work [3], boundaries between the sigma phase and residual ferrite are also convenient nucleation sites for the re-formation of ferrite upon heating above 1173 K.

Effect of annealing duration

Effect of annealing duration on the sigma phase (before DTA measurements)

At a fixed temperature, the sigma phase of the samples annealed for different durations exhibited different morphologies (Fig. 2) and coarsened continuously (Table 2). At first, the ferrite decomposed into a fine, interconnected eutectoid structure comprising the sigma phase and secondary austenite (Fig. 2a), then the sigma phase coarsened as annealing proceeded (Fig. 2b).

Although the morphology and size of the sigma phase of the samples annealed for different times were different, the enthalpy of dissolution stayed nearly constant (Table 2). This implies that over 168 h at 973 K, the total quantity of the sigma phase did not change much, in agreement with the results obtained from quantitative metallography (Table 2). EDS revealed that the composition of the sigma phase stabilised at the early stage of annealing (Fig. 3). These results have demonstrated that at the later stage of annealing, the change of the sigma phase was mostly morphological. As the characteristic temperatures obtained from DTA measurements kept changing up to at least 3000 h (to be discussed below), the early stabilisation of

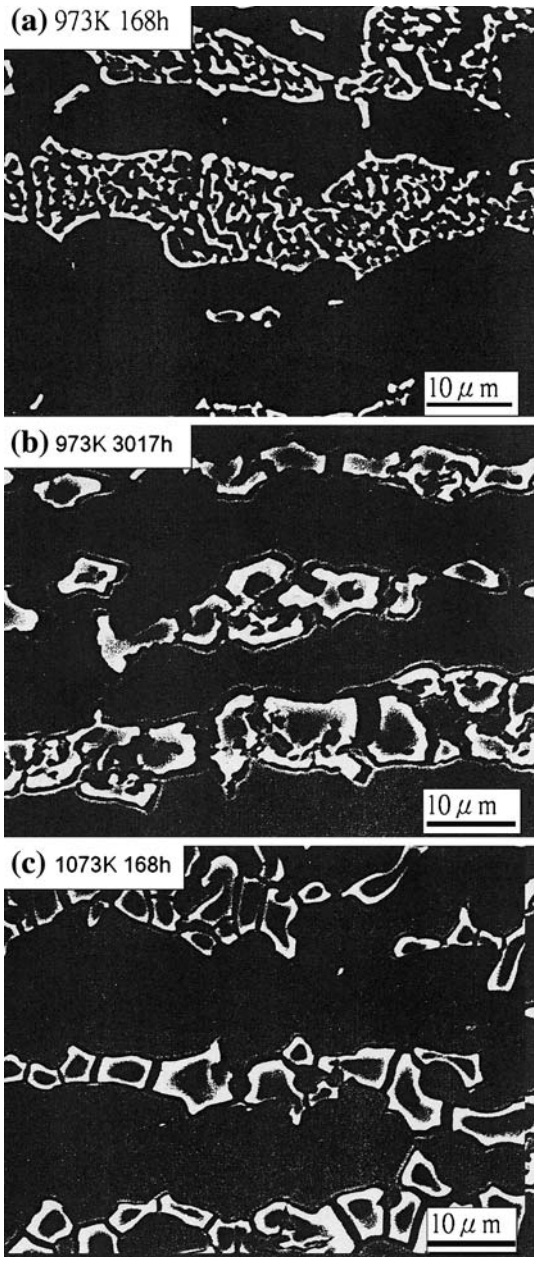

Fig. 2 Morphologies of the sigma phase for different annealing conditions (partly reproduced from [3])

Table 2 Average values of the longest dimension, enthalpy of dissolution and area fraction of the sigma phase of samples annealed at 973 K for different times

Annealing duration (h)	168	1000	3017
Diameter (μm)	0.87	1.32	1.58
Enthalpy (J/g)	5.643	5.704	5.508
Areal fraction (%)	26.41	27.01	26.32[a]

[a] Samples annealed for 2980 h

composition implies that the effect of composition on the dissolution of the sigma phase and the re-formation of ferrite is not high.

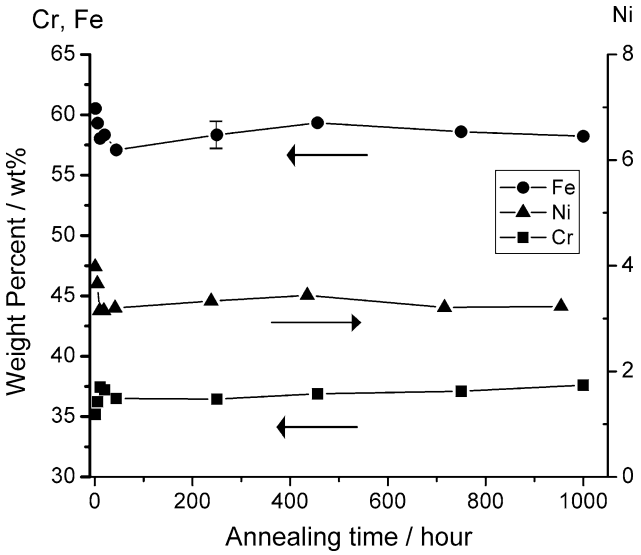

Fig. 3 Results of EDS of the sigma phase of samples annealed at 973 K (the error bar indicated is representative of other data points. Only one error bar is shown for clarity)

Effect of annealing duration on DTA measurements

The sigma phase obtained after annealing for different durations behaved differently in DTA measurements as follows: the reversion of sigma to ferrite at high temperatures is endothermic (Fig. 4). For the samples annealed at 973 K for different times, Figs. 4 and 5 show that both the extrapolated onset temperature (T_s) and the peak temperature (T_p) shifted upwards as annealing proceeded.

Inasmuch as the composition of the sigma phase nearly stabilised at about 50 h upon annealing at 973 K (Fig. 3), but both T_s and T_p kept changing up to at least 3017 h (Fig. 5), it may be inferred that the effect of composition on T_s and T_p was not significant.

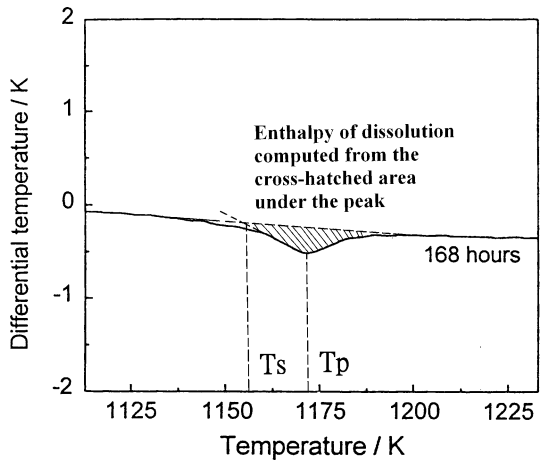

Fig. 4 A representative DTA thermogram for the dissolution of the sigma phase

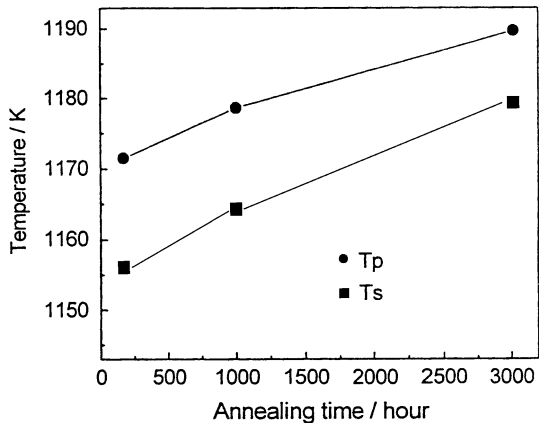

Fig. 5 T_s and T_p of the sigma-to-ferrite transformation for samples annealed at 973 K for different durations (40 K/min)

Effect of annealing temperature

Effect of annealing temperature on the sigma phase (before DTA measurements)

At a fixed annealing duration, as annealing temperature increased, the sigma phase grew bigger (Table 3; Fig. 2a, c). However, its composition changed only a little with temperature (Table 4). This table indicates the compositions of samples annealed at different temperatures for 456 h. At this time, the compositions of the samples had already stabilised (refer to Fig. 3). Also, Cr tended to segregate to the sigma phase, in agreement with the results of Swens' [12] and Cortie's [13]. Between 973 and 1123 K, the phase diagrams of the Fe–Cr–Ni alloy [9] show that the phase boundaries only displace slightly, and so the compositions of the various phases will only change slightly with temperature.

Table 3 Longest dimension (μm) of the sigma phase of samples that were annealed differently

	168 h	1000 h	3017 h
973 K	0.87	1.32	1.58
1023 K	1.45	2.44	3.37[a]
1073 K	3.21	3.79	4.01

[a] Value from samples annealed for 2980 h

Table 4 Results of EDS (wt%) of the sigma of samples annealed at different temperatures for 456 h

	Cr	Fe	Ni
973 K	36.89	59.34	3.44
1023 K	38.10	56.08	3.43
1073 K	40.50	55.55	3.56

Only results for the major alloying elements are shown

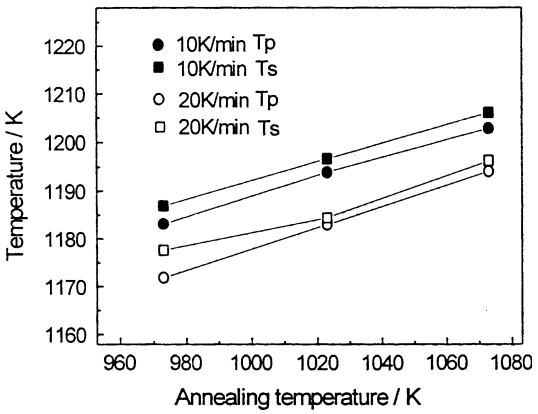

Fig. 6 Effects of annealing temperature on the onset temperature (T_s) and peak temperature (T_p) (samples annealed for 168 h)

Effect of annealing temperature on DTA measurements

The sigma phase obtained after annealing at different temperatures behaved differently in DTA measurements as follows: the T_s and T_p of samples annealed at 973, 1023 and 1073 K for 168 h are shown in Fig. 6. It can be seen that both T_s and T_p increase with increasing annealing temperature, irrespective of heating rates.

Even though Table 4 shows that the composition of the sigma phase was dependent upon temperature, it is believed that the changes of only a few weight percents in Fe, Cr and Ni would not have a pronounced effect on T_s and T_p. The effect of composition on T_s and T_p can, therefore, again be viewed as secondary to that of morphology.

Discussion

It has been demonstrated that the morphology, growth kinetics, composition and size of the sigma phase are dependent upon its annealing temperature and duration. These factors in turn sensitively affect T_s and T_p of the sigma-to-ferrite transformation. Therefore, the present study has demonstrated that it may be viable to monitor the coarsening and morphological evolution of the sigma phase by using thermal analysis.

Referring to Fig. 3, one can see that the composition of the sigma phase nearly stabilised at about 50 h upon annealing at 973 K, but both T_s and T_p kept changing up to at least 3017 h (Fig. 5). Consequently, it may be inferred that the effect of composition on T_s and T_p is not significant.

Excluding the effect of composition, one can explain the dependence of T_s and T_p on annealing duration and temperature (Figs. 5, 6) on grounds of the different morphologies of the sigma phase and the presence of untransformed ferrite as follows: both TEM observation (Fig. 1) and magnetic tests (Table 1) revealed that there was untransformed ferrite in the annealed samples. During DTA measurements, the untransformed ferrite served as 'ready nuclei' for the sigma-to-ferrite transformation, thereby reducing the degree of overheating (ΔT), which provides the driving force for nucleation, needed to kick-start sigma dissolution. The higher the amount of untransformed ferrite, the lower the value of ΔT will be. In turn, a lower value of ΔT means that the transformation may begin at a lower temperature, thereby leading to a lower T_s in DTA measurement.

As annealing proceeded, more untransformed ferrite underwent transformation to the sigma phase and secondary austenite. Therefore, when compared with those annealed for 168 h, samples annealed for 1000 h contained less untransformed ferrite. In addition, less grain boundaries, and hence less available nucleation sites for the sigma-to-ferrite transformation during DTA measurement, were present in the samples annealed for 1000 h because the sigma phase had coarsened (compare Fig. 2a, b). Reductions in the amount of untransformed ferrite and grain boundaries heightened the barrier to dissolution for the sigma phase of the samples annealed for 1000 h. Hence, the degree of overheating required to initiate the sigma-to-ferrite transformation during DTA measurements was raised, thereby increasing the T_s for samples annealed for 1000 h. The further increase in T_s for samples annealed for 3017 h could be explained on similar grounds (Figs. 5, 6).

T_p is the temperature at which the evolution of heat of reaction/transformation is the most intense [14]. Although not necessarily the same, some authors regard T_p as the temperature at which the transformation rate is the highest [15–17]. Over T_p, the transforming phase shall undergo transformation rapidly [16]. In the present work, T_p would thus denote the temperature over which the sigma phase dissolves rapidly. The sigma phase of the samples annealed for 3017 h at 973 K were bigger than those of the samples annealed for 168 h (compare Fig. 2a, c). The bulkier sigma phase would thus take longer and be harder to dissolve completely. Hence, during DTA measurements, fast dissolution of the bulkier sigma phase of the samples annealed for 3017 h would be more difficult to attain, thereby shifting T_p upwards (Figs. 5, 6).

As to the effect of annealing temperature, it is obvious in Fig. 6 that both T_s and T_p are directly proportional to the annealing temperature. Again, this may be attributable to the fact that for the samples annealed at higher temperatures, they got less untransformed ferrite, but bulkier sigma phase (and so less grain boundary) (compare Fig. 2a, c and refer to Table 3). These all served to raise the barrier to the sigma-to-ferrite transformation for samples annealed at higher temperatures, thereby raising their values of T_s and T_p.

Potential application for temperature monitoring

Potentially, the combination of DTA and duplex stainless steel may provide a means for temperature monitoring between 873 and 1173 K where the sigma phase forms. The method works as follows: first, a small piece of duplex stainless steel is attached intimately to a component whose working temperature is to be determined (so, the stainless steel piece and the component are in close thermal contact); second, after a certain period of time, the stainless steel piece is detached from the component (hence, the annealing duration of the stainless steel piece is known); third, the T_s and T_p of the stainless steel piece are measured by using DTA; fourth, a calibration graph like Fig. 6 is used to deduce the prior annealing temperature of the stainless steel piece. Alternatively, if the working temperature of the component is known and one wants to determine for how long the component has worked at this temperature, then one can follow the same steps listed above and use a calibration graph like Fig. 5. This method of temperature measurement is similar to other well-established techniques that also utilise phase transformations, such as the Feroplug [18] and the Templug [18].

It has to be emphasised that the proposed method for measuring temperature is still in its infancy. And work is underway to assess its accuracy and resolution. Nevertheless, a strength of this method is that it may be used for rough measurement of the prior working temperature of components that operate in hostile environments, because the 'temperature sensors' are just duplex stainless steels (so they may be deployed to corrosive and high-temperature environments). Unlike conventional techniques like thermocouples, the current method involves no clumsy connecting cables and therefore is deployable to moving, rotating parts. Furthermore, this method is not expensive. Therefore, although it might not give very high accuracy, it may be used to complement other methods.

Conclusions

The present work has shown that it may be viable to use thermal techniques like DTA to monitor the growth and morphological evolution of the sigma phase. Potentially, DTA may be used to for temperature monitoring of components working between about 873 and 1173 K.

As annealing proceeds at a fixed temperature, the morphology and size of the sigma phase change constantly, but its total quantity stays more or less unchanged. The characteristics of DTA peaks, i.e. T_s and T_p, are very sensitive to the morphological evolution of the sigma phase. At a fixed temperature, as annealing proceeds, both T_s and T_p gradually shift upwards. At a certain annealing time, T_s and T_p will also shift upwards in proportion to annealing temperature.

The boundaries between austenite and the sigma phase were suggested to be one of the reasons for the upward shift in Ref. [3]. The present work has demonstrated that the boundaries between untransformed, residual ferrite and the sigma phase may also play a part. The untransformed ferrite serve as ready nuclei for the sigma-to-ferrite transformation upon heating. As annealing goes by with time, the sigma phase coarsens and so less grain boundary was present. Also, more untransformed ferrite will undergo transformation to the sigma phase, leading to a reduction in the number of ready ferrite nuclei. These factors raise the barrier to the sigma-to-ferrite transformation and so shift T_s upwards. As regards annealing temperature, the sigma phase becomes bulkier and less untransformed ferrite would be available as temperature goes up. So, the amount of grain boundary that can act as favourable nucleation sites for the sigma-to-ferrite transformation is reduced. Hence, the barrier for transformation is heightened as the annealing temperature increases, which then leads to an increase in T_s. The effect of compositional change on T_s and T_p is not high, thus disproving the conjecture in reference [3]. Instead, these temperatures are more related to the morphological evolution of the sigma phase.

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