B2-intermetallic phase characterization in a ferritic Fe-Cr-Ni-Mn-Al-C steel

RAHIMI Reza 1, PEKKER Péter 2, BIERMANN Horst 3, MOLA Javad 1

(1. Institute of Iron and Steel Technology, Technische Universität Bergakademie Freiberg, Germany
2. Institute of Metal Forming Science and Nanotechnology, University of Miskolc, Hungary
3. Institute of Materials Engineering, Technische Universität Bergakademie Freiberg, Germany)

Abstract: The unexpected increase in the apparent coefficient of thermal expansion (CTEₐ) of a ferritic Fe–Cr–Ni–Al–Mn–C stainless steel was investigated. This anomaly was ascribed to the dissolution of fine (Ni,Fe)Al precipitates with B2 crystal structure upon continuous heating. The increase in the CTEₐ during the dissolution of B2 precipitates was attributed to the lattice expansion of the ferritic matrix. Accordingly, the end of B2 dissolution was associated with a decrease in the CTEₐ. This was confirmed by microstructure examination of samples quenched from different temperatures.

Key words: Al-alloyed steels, stainless steels, CTE, B2 intermetallic, TEM

Al-alloyed steels offer an excellent combination of strength and ductility. As a result, many investigations have been performed to develop Al-alloyed steels with UTS × elongation values exceeding 60,000 MPa.% [1]. The primary advantage of Al-alloyed steels is their reduced density and their raised specific strength. For Fe–Mn–Al–C alloys containing up to 12 mass-% Al, reduction in the specific weight of the order of 1.5% has been reported by the addition of each 1 mass-% Al [2]. An important application area for Al-alloyed lightweight steels is in the automobile industry where lighter components can reduce the fuel consumption and emissions [3].

In view of the discussed benefits, the addition of higher amounts of Al is well justified. In practice, however, Al addition into steels is limited due to the precipitation of brittle intermetallic phases such as FeAl and Fe₃Al. The occurrence of ordered intermetallic compounds may generally lower the ductility of steels and restrict their application [4]. For instance, a drastic embrittlement in Fe–Al–Mn steels has been observed after introduction of 10.5 mass-% Al [5]. Nevertheless, high strength low density steels with high ductility have been recently developed in which intermetallics serve as the strengthening second phase [6]. Accordingly, a precise understating of the alloying concept and the identification of the constitutional phases are of great interest.

This work was initiated after the observation of abnormally high CTEₐ values during dilatometry heating of the experimental alloy. In order to understand the reason behind the observed CTEₐ variations, the microstructure was investigated by electron microscopy methods. The results lead to a better perception of the nature of the intermetallic precipitates in Ni- and Cr-containing Al-alloyed steels.

1 Experimental Methods

Al-alloyed steel with the chemical composition shown in Table 1 was cast in a vacuum induction melting furnace. The cast ingot was homogenization treated at 1200 °C for 1 h. Cooling rate was 2.5 °C/s in the temperature range 1200-600 °C. Samples were subsequently characterized by light optical microscopy, scanning electron microscopy using a Zeiss Ultra 55 type field emission microscope (FESEM), transmission electron microscopy using an FEI Tecnai G2 type transmission electron microscope (TEM), and X-ray diffraction (XRD) with a Cu anode (λ= 0.154060 nm). Dilatometry studies using 3.5 × 3.5 × 10 mm³ samples were done in a BÄHR-DIL805 dilatometer. Heating and soaking steps were done in vacuum. Cooling was done by argon flow into the chamber. Heating and cooling rates in dilatometry cycles were 50 °C/s and 20 °C/s, respectively.
2 Results and discussion

The steel exhibited a high density of cracks after homogenization heat treatment (Fig. 1). This indicated the brittle nature of the alloy, likely as a consequence of a precipitation reaction. Fig. 2(a) shows the first derivative of dilatometry curves in the heating segment. CTEₐ irregularities occur near the Curie temperature (Tₑ) due to the ferromagnetic to paramagnetic transition of ferrite [7]. Tₑ in the homogenized condition is about 477 °C. Above Tₑ, an unusual CTEₐ rise was observed. The abnormality in the CTEₐ becomes clear after a comparison with that of an Al-free Fe–18 mass-%Cr steel (Fig. 2(a)). Although CTEₐ variations in both steels initially follow the same trend, a significant divergence occurs above Tₑ of the Al-alloyed steel where it exhibits a CTEₐ almost 1.5 times that of the binary alloy at 990 °C. As shown in the inset of Fig. 2(a), the abnormality was highly reversible and also occurred in the cooling step.

Fig. 1 Example of macro-cracks in the as-homogenized ingot

Fig. 2(b) shows CTEₐ changes around Tₑ for two differently cooled specimens of the Al-alloyed steel where the brine-quenched specimen (higher cooling rate) exhibits a lower Tₑ than the homogenized specimen. This suggests the presence of a higher solute content after brine quenching. In other words, the occurrence of a precipitation reaction in the as-homogenized steel might have led to a depletion of the solute substitutional content of ferrite.

In order to justify the abnormal CTEₐ rise, the microstructure was characterized by microscopy and XRD techniques. Figs. 3(a)-(c) show the as-homogenized microstructure at two different magnifications and the corresponding XRD profile. The coarse precipitates in Fig. 3(a) were identified by XRD to be M₇C₃ carbides, where M mainly denotes Fe, Cr, and other substitutional alloying elements [8]. According to Fig. 3(b), a significant fraction of fine precipitates exists in the matrix. Further TEM examinations revealed a bimodal distribution of precipitates in the matrix (Fig. 4(a)). Selected area diffraction (SAD) analysis demonstrated that the precipitates distributed in the α-ferrite were aluminides with a CsCl B2 crystal structure. The orientation relationship between precipitates and the matrix was cube-on-cube, namely (011)ₐ // (011)ₐ and [011]ₐ // [011]ₐ. The fast Fourier transformation analysis performed on the area marked by a square in the high resolution TEM micrograph of Fig. 4(f) indicated that the finer precipitates too were B2 intermetallics.

The presence of a considerable fraction of hard B2 intermetallics in the present alloy justifies the high hardness (420 HVₐ) as well as the occurrence of cracks after the homogenization heat treatment. The presence of hard B2 intermetallics appear to have reduced the ability of the alloy to accommodate the thermally-induced stresses. Similarly, during tensile tests (not shown), fracture occurred in the elastic deformation range.

The TEM-SAD-based differentiation of ordered D₀₃ and B2 structures in Al-alloyed steels is explained in the following. Since D₀₃ structure is a superlattice, its reciprocal lattice includes both B2 and α reflections. The lattice parameter of D₀₃ (aD₀₃ = 5.7934 Å) is almost double that of B2 (aB₂ = 2.8954 Å) leading to the superposition of its (2h 2k 2l) diffraction spots on the (h k l) spots of B2/ferrite. Therefore, the SAD patterns of D₀₃ with any of the [111], [100], or [120] zone axes would be identical to the corresponding B2 SAD patterns except that the D₀₃ indices are double that of B2. In other words, when the zone axis of D₀₃ is such that the diffraction spots all have even (h k l) indices, the SAD pattern may also be attributed to the B2 and a differentiation would not be possible. For instance, the SAD pattern in Fig. 4(b) may be indexed according to both D₀₃ and

| Table 1 Chemical composition of the experimental Al-alloyed steel |
|-------------------|---|---|---|---|---|---|---|---|
| Element | C | Al | Mn | Cr | Ni | Si | Fe/others |
| Mass-% | 0.46 | 7.07 | 6.25 | 17.08 | 8.72 | 0.39 | balance |
B2 solutions. Differentiation is only possible when the zone axis is such that the suspected D0\textsubscript{3} SAD pattern consists only of odd \((h k l)\) indices [9]. When both D0\textsubscript{3} and B2 phases are present, the identification can be done by dark field imaging. In this case, D0\textsubscript{3} reflections with odd indices do not have equivalents in the corresponding B2 pattern [10].

The SAD patterns taken from a precipitate and the surrounding matrix as marked by circles in Fig. 4(a) are shown in Figs. 4(b) and (c), respectively. Based on the previous discussion, the [010] zone axis SAD pattern in Fig. 4(b) fits to both D0\textsubscript{3} and B2 phases (D0\textsubscript{3} indices are all even). In order to enable a differentiation, SAD pattern was recorded from the [011] zone axis. In this zone axis, the characteristic \((111)\) reflections of D0\textsubscript{3} do not coincide with any of the B2 spots. If the SAD pattern in Fig. 4(d) were to be for the D0\textsubscript{3} phase, one would expect to observe extra spots from \((111)_{D03}\) halfway between the incident beam and the spots marked \((111)_{B2}\). Therefore, the possibility of precipitates being D0\textsubscript{3} can be excluded.

The absence of D0\textsubscript{3} is the present case may be attributed to the high Ni content of the steel. In contrast to Cr which promotes the occurrence of D0\textsubscript{3} [11], Ni addition can stabilize B2 [6,12]. The TEM-EDS analysis result for the matrix and a coarse precipitate is given in Fig. 4(g). It confirms that the Ni content of precipitates is higher than their Fe content. Therefore, the precipitates can be denoted (Ni,Fe)Al. Replacing Fe by Ni at a constant Al content has been reported to decrease the formation enthalpy of B2 \((Fe,Ni)\textsubscript{1-x}Al\textsubscript{x}\) precipitates thereby favoring the formation of Ni-rich \((Fe,Ni)Al\) precipitates [13].

Fig. 2 (a) CTE\textsubscript{a} values during dilatometry heating between 150–1150 °C. The inset shows the reversibility of the anomaly upon heating and cooling; (b) shift in the \(T_c\) temperature after two different cooling schemes.

![Diagram](image1)

Fig. 3 (a) Optical micrograph showing an overview of the microstructure; (b) microstructure of the same specimen observed at a higher magnification by SEM; (c) XRD profile in the as-homogenized condition. The specimens for metallography were electro-etched in pure HNO\textsubscript{3}.  

![Diagram](image2)
Based on the microstructural examinations, the unusual CTE\textsubscript{a} variation can be justified by the dissolution of existing B2 intermetallics. In order to study the dissolution of precipitates, samples were heat treated at 800 °C and 1100 °C and then quenched in water to freeze the microstructure. As shown in Fig. 5, the microstructure after quenching from 800 °C, which is well below the CTE\textsubscript{a} maximum at 990 °C, is very similar to the microstructure after homogenization treatment. At 1100 °C, which is above the CTE\textsubscript{a} maximum and the subsequent CTE\textsubscript{a} decrease, no precipitates were found in the microstructure. The high CTE\textsubscript{a} values between 800 °C and 1055 °C are therefore ascribed to the lattice expansion of ferrite as B2 precipitates dissolve into the matrix and enrich it with respect to Al and Ni. An increase in the solute content of both elements, particularly Al, increases the lattice parameter of ferritic steels [19,20]. The rate of lattice expansion due to the introduction of Al and Ni into ferrite was high at temperatures up to 990 °C. Afterwards, it decreased until the dissolution end temperature of approximately 1050 °C was reached. At higher temperatures, the CTE\textsubscript{a} remains above that of the reference Fe-18 mass-%Cr steel which might be related to the vacancy formation in the ferrite whose Al content then becomes equal to the nominal Al content of the alloy.

Fig. 4 (a) Bright field image of the Al-alloyed steel; (b) and (e) are the SAD patterns taken from the precipitate and the matrix region marked by circles in (a), respectively; (d) and (e) are the SAD patterns taken from the [011] zone axis; (f) high resolution image of one of the fine precipitates in the matrix and the fast Fourier transformation of the region marked by a square; (g) TEM-EDS spectra of the matrix and a precipitate.
3 Conclusions

The unexpected high CTE$_a$ values for a ferritic Fe–Cr–Ni–Al–Mn–C stainless steel in the temperature range of 800-1050 °C was justified by the dissolution of the existing B2 intermetallics of the type (Ni,Fe)Al.

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