



Manganese micro-segregation governed austenite re-reversion and its mechanical effects

Meimei Wang^{a,b,1}, Menglei Jiang^{a,1}, Cemal Cem Tasan^{a,*}

^a Department of Materials Science and Engineering, MIT, 77 Mass. Avenue, Cambridge, MA 02139 USA

^b Max-Planck-Institut für Eisenforschung, Max-Planck-Straße 1, 40237 Düsseldorf, Germany

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ABSTRACT

Martensite that is mechanically induced from reverted austenite can be reverted again to austenite upon annealing. Carrying out mechanical tests, electron backscatter diffraction, electron channeling contrast imaging, and energy-dispersive X-ray spectroscopy analyses, we observe that Mn micro-segregation governs this re-reversion process in a martensite-reverted-austenite steel. The annealing treatment cannot fully revert all strain-induced effects in this multi-phase alloy (i.e., ductile damage, grain shape change) and introduces some new changes (e.g. precipitate size in martensite). However, the resulting microstructure exhibits the original mechanical response even after multiple reversions, demonstrating the governing role of the mechanically induced martensitic transformation on strain hardening.

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Austenite reversion is often introduced to design steels with enhanced mechanical properties [1–7], and thus the dependence of the reverted austenite behavior on microstructural characteristics has been of considerable research interest [8–19]. Two main transformation mechanisms are proposed for the reverse transformation: (i) diffusional [10], which is observed upon low temperature, long-duration annealing; and (ii) diffusionless [20], which typically takes place under the opposite conditions [21]. The former leads to the nucleation of low defect density austenite grains at grain boundaries, whereas the latter leads to reverted austenite with high defect density and with a specific crystallographic orientation relationship to the parent martensite. The activity of defects during austenite reversion is thus critical from a mechanistic perspective. Here, we investigate a Fe–9Mn–3Ni–1.4Al–0.01C (mass%) martensite-reverted austenite transformation-induced plasticity (TRIP) – maraging steel, to improve our understanding of austenite re-reversion from martensite and its resulting mechanical effects. With re-reversion, we refer to the case where the austenite is reverted from martensite during an initial annealing treatment, then deformed to trigger its mechanically induced martensitic transformation, and then annealed again to revert to austenite. Thus, the main difference between reversion and re-reversion is expected to be the crystallographic defect density prior

to the annealing treatment, and the effects of chemical patterning [7,22].

Samples of TRIP-maraging steel are hot rolled, homogenized, and then annealed at 600 °C for 8 h (i.e. the reversion treatment) to create the starting martensite-reverted austenite microstructure (Fig. 1a). This treatment also leads to precipitation in martensite, as in classical maraging steels [4]. The austenite is metastable, exhibiting both TRIP and twinning-induced plasticity (TWIP) [4] effects, both of which are size-dependent [23]. The microstructure development in this steel during thermal processing [1,5] and deformation [4,5,23] are reported previously.

To study the re-reversion transformation, tension test samples (cut along the rolling direction using electrical discharge machining) are deformed up to different levels of engineering strain (5%, 10%, 13%). Each sample is then removed from the testing rig and heat-treated under an argon atmosphere (i.e. the re-reversion treatment). These annealing treatments are carried out at 600 °C for different durations, but the results shown here are those of the 8 h treatments. Following the heat treatment, each sample is placed back in the tension rig again for further straining. This process is repeated a maximum of two times in this study. Various characterization techniques are employed for microstructure analyses at original, deformed, and the annealed states, including secondary electron (SE) imaging, electron backscattering diffraction (EBSD), electron channeling contrast imaging (ECCI), X-ray diffraction (XRD) and energy dispersive X-Ray spectroscopy (EDS). EBSD measurements are carried out in JEOL JSM-6500F with an acceleration voltage of 15 kV, a working distance of 16 mm, and

* Corresponding author.

E-mail address: tasan@mit.edu (C.C. Tasan).

¹ These authors contributed equally.

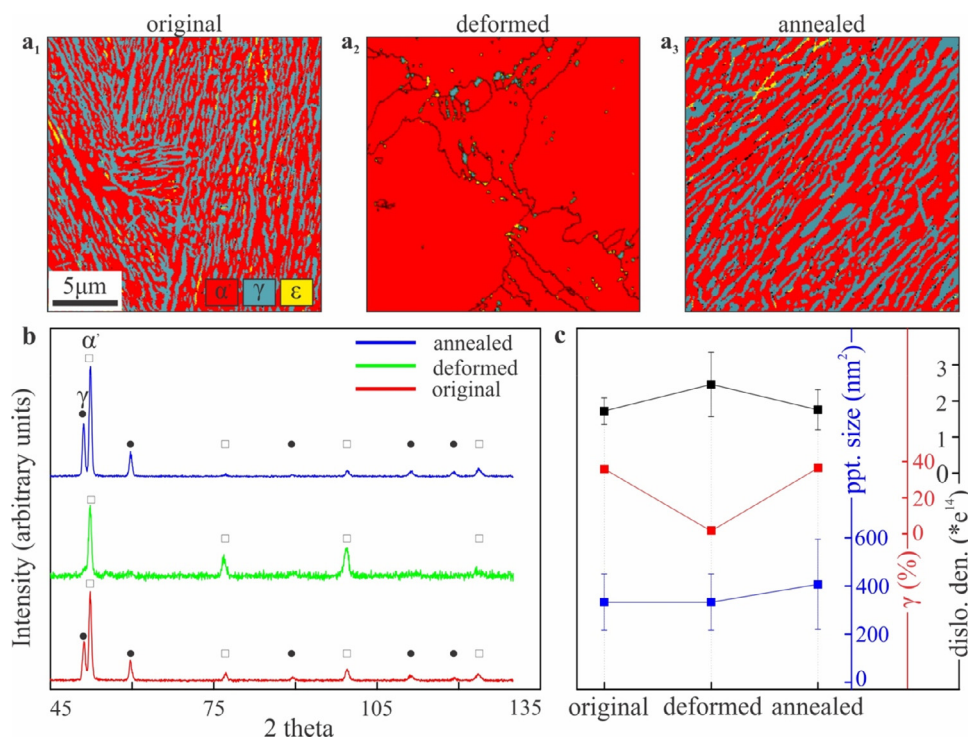


Fig. 1. Annealing reverts deformation-induced microstructure changes: (a) EBSD phase maps and (b) XRD measurements of the TRIP-maraging steel at the (a₁) undeformed, (a₂) 10% deformed and (a₃) annealed states. (c) Martensite dislocation density (ECCI), martensite precipitate size (ECCI), austenite fraction (EBSD) are shown at different states. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

a step size of 80 nm. ECCI measurements are conducted in Zeiss-Merlin SEM with an acceleration voltage of 30 kV and a current of 4 nA under optimized diffraction conditions. XRD measurements are conducted using XRD3003 Theta/Theta Seifert Analytical X-ray (GE Inspection Technologies) with a Co target ($\lambda=1.78897\text{e-}10$ m) and analyzed with Maud software.

Prior to deformation, the microstructure of original sample consists of α' martensite (phase in red), nanoscale reversed austenite (phase in blue) and a small fraction of ε martensite (3%, phase in yellow) (Fig. 1a₁). Austenite grains decorate prior γ grain boundaries and martensite packet, block and lath boundaries. When this steel is strained in uniaxial tension, the austenite fraction decreases from ~37% to ~0%, after 10% deformation [4]. The average austenite grain size decreases from $0.31\text{ }\mu\text{m}^2$ to $0.15\text{ }\mu\text{m}^2$ [4] (from $30\text{ }\mu\text{m} \times 60\text{ }\mu\text{m}$ EBSD scans). Upon the annealing treatment, the austenite content goes back to ~40% (annealed state, Fig. 1a₃), and the grain size goes back to $0.31\text{ }\mu\text{m}^2$. The mechanically induced martensite transformation, and the re-reversion are also demonstrated by XRD measurements (Fig. 1b). After 15% deformation, almost all γ peaks vanish, and α' martensite peaks become wider, indicating completion of martensite transformation and increase in dislocation density of α' martensite at the same time (green profile). After re-reversion, γ peaks reappeared, and α' martensite peaks reset to their original peak width as in original state, implying the simultaneous restoration of γ phase and dislocation density in martensite (blue profile).

The return of the austenite fraction to its original levels after the 8hr re-reversion treatment is expected since this treatment is carried out at the same annealing temperature of the reversion treatment, and thus follows the same thermodynamic equilibrium conditions. But the maintenance of the nano-laminate structure (i.e. the re-reverted austenite grains are located again at various lath martensitic boundaries (Fig. 1a₃)) is worth more consideration and will be discussed in more detail below (Fig. 3). Focusing on the martensite, the ECCI analyses (Fig. S1) [24] reveal the

deformation-induced increase in dislocation density, which is then recovered during the final annealing treatment (Fig. 1c). The dislocation density in martensite increases from $17.1 \pm 3.7 \times 10^{15}\text{m}^{-2}$ in the original state (martensite matrix) to $24.5 \pm 8.9 \times 10^{15}\text{m}^{-2}$ in 8% deformed state (martensite matrix + mechanically induced martensite), but the annealing treatment decreases it back to $17.4 \pm 3.6 \times 10^{15}\text{m}^{-2}$ (mainly martensite matrix, explained later). The austenite grains in this alloy accommodate strain by formation of stacking faults, mechanical twinning and transformation into martensite [4] (Figs. S1a₂ and S1a₃). The mechanically induced martensite has high dislocation density caused by phase transformation [25]. After annealing, mechanically induced martensite reverts to austenite during re-reversion process, which decreases dislocation density of martensite phase. In some grains, it can be observed that the re-reverted austenite grains inherit the deformation substructure, i.e. stacking faults and twin boundaries, suggesting a shear governed re-reversion process (Fig. S1b₁) [11]. For martensite matrix, the similar dislocation density at undeformed and annealed state suggest that the multiplication of dislocations during deformation [4,26] and annihilation of dislocations during succeeding annealing treatment [27] are approximately balanced.

Note that, not all the deformation-induced changes in the microstructure are removed upon the final annealing treatment: (i) the small increase in the average ductile damage size ($\sim 0.1\text{ }\mu\text{m}^2$ [4]) cannot be influenced by the re-reversion thermal treatment [28]; (ii) plastic deformation induced changes in the aspect ratio of the microstructural constituents, are also not affected from the final annealing, and (iii) plastic deformation induced grain rotation and texture developments are not expected to be perfectly reverted [4,29,30]. Moreover, new (and subtle) changes are introduced upon annealing, for example, the average size of the martensite precipitates slightly increases from $356 \pm 1\text{ nm}^2$ to $430 \pm 2\text{ nm}^2$ upon annealing (Figs. 1c and S1), although the precipitate number density is not changed.

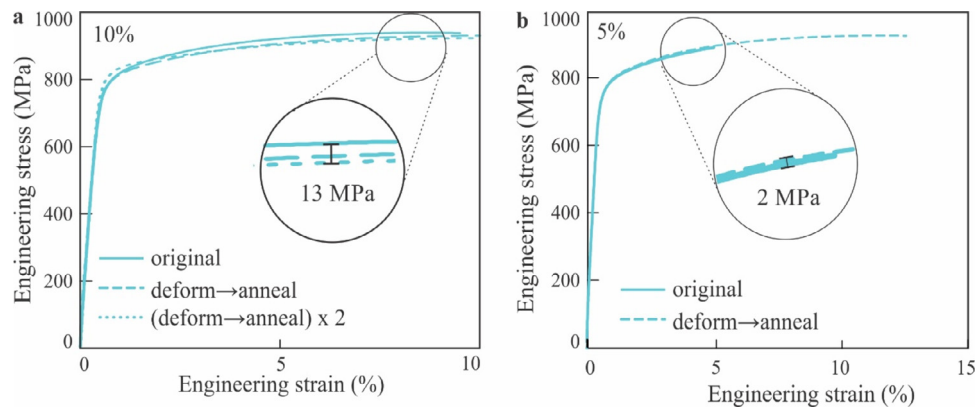


Fig. 2. Annealing reproduces the mechanical response of TRIP-maraging steel: (a) Engineering stress-strain curves of the original, annealed, and double-annealed TRIP-maraging steel are effectively on top of each other; (b) Engineering stress-strain curves of the re-reverted microstructure with pre-strain at 5%.

The results of the uniaxial tensile tests are shown in Fig. 2. Focusing first on the case of 10% pre-strain, it is clear that the application of the re-reversion treatment leads to a near-perfect overlap of the stress-strain curves with a maximum deviation of only $\sim 1.5\%$ of σ_{UTS} (Fig. 1a). Even when the second cycle of 10% deformation and annealing is applied, the stress-strain curve still effectively follows the original curve. The recovery of the same overall strain hardening response demonstrates that the strain hardening contributions due to the mechanically-induced martensitic transformation of the austenite, and plasticity of martensite, are also recovered. These correspond well with the observed recovery of the nano-laminated microstructure morphology, phase fractions, and defect structure in both phases discussed in Fig. 1. The metastability of austenite phase highly depends on its defect structure [23]. Apparently, the microstructural changes that are not reverted by annealing (listed in the previous paragraph) or those changes that are introduced by annealing have a relatively small influence on the mechanical response of this material.

To study the influence of pre-strain level on the reverse transformation, 5% (Fig. 2b) and 13% (Fig. S2) pre-strain are also applied. The accumulation of damage at this early stage of deformation would be limited [4], yet still increases as the pre-strain level increases. The annealing temperature is below the melting point, and thus, the annealed sample inherits the damage incidents, which would contribute to strain localization and early failure. The increased pre-strain level also influences the re-reversion kinetics and thus can alter the volume fraction and meta-stability of re-reverted austenite. However, similar to the case of 10% pre-straining, when pre-strain is decreased to 5%, the stress-strain curves again exhibit near-perfect overlap (See Fig. 2b). When the pre-strain level increases to 13% (Fig. S2), which is slightly beyond the strain level for plastic instability, the shape change cannot be fully removed. Apparent decreases in uniform elongation and total elongation are observed.

In most multi-phase alloys, each phase has different characteristic mechanical and thermal stabilities [31–33], and hence, they respond differently to applied mechanical and/or thermal boundary conditions. As a result, near-perfect microstructure reversion would typically require complicated heat treatments. The microstructure characterization in Fig. 1, and the mechanical tests in Fig. 2 reveal that, within a certain level of change in pre-strain level (Fig. 2), the properties of the multi-phase TRIP-maraging steel are recovered almost perfectly to their original state with a single step annealing treatment, similar to simple single-phase microstructures where only recovery or recrystallization treatments are sufficient for this purpose [34]. Next, two key characteristics of the present two phases [4] are discussed, which we propose to

govern this easy recovery of the original mechanical behavior: (i) Mn micro-segregation in the austenite (Fig. 3a); and (ii) the high density of nano-precipitates in martensite (Fig. 3b), both of which arises due to the initial reversion treatment prior to mechanical deformation.

In this alloy austenite is stabilized by the Mn segregation at martensitic boundaries during the first reversion treatment (Fig. 3a₁). At low deformation levels, the plastic strain is mainly accommodated by the mechanically induced martensitic transformation of the austenite [35]. This is a shear dominated and diffusionless transformation, and thus, it has a negligible influence on the micro-segregation or distribution of the Mn in the austenite regions (Fig. 3a₂). Thus, the micro-segregated Mn still stabilizes the austenite upon the post-deformation annealing treatment [35], causing austenite re-reversion where austenite was previously located before deformation (Fig. 3a).

On the other hand, in the martensite matrix, first reversion treatment induces (maraging) precipitates. These are observed to pin dislocations both during deformation and during recovery treatments (Fig. 3b) [36,37]. Since the majority of the macroscopic strain is accommodated by austenite at 10% strain, dislocation accumulation in martensite matrix during deformation is limited (Figs. 3b, 1c and S1). Due to the presence of maraging precipitates, dislocation recovery is limited in martensite matrix during the re-reversion treatment, as well (Figs. 3b, 1c and S1). As shown in the insets of Fig. 3b, the nano precipitates effectively hinders the change in dislocation density during both deformation and annealing and enables the material to maintain its UTS after annealing (Fig. 2a).

The austenite from initial reversion, and from the re-reversion treatment differ in their need for Mn diffusion. In segregation governed austenite reversion, the free energy difference between boundaries and bulk is the driving force [38,39], the martensite matrix acts as an active Mn reservoir, and the dislocations provide a Mn diffusion pathway for the austenite reversion [38]. The morphology, location, and size of austenite regions depend on boundary characteristics, annealing temperature, and annealing time [10,40]. Given the grain size [23,41], boundary condition [42], and stacking fault energy [4,43] dependences of austenite metastability, austenitic steel can exhibit a wide variety of mechanical properties after segregation-induced austenite reversion.

In re-reversion, on the other hand, Mn segregation already exists, and no long-range diffusion is needed for austenite re-reversion in the mechanically induced martensite region [4]. The diffusion coefficient of Mn is smaller compared to interstitial austenite stabilizers, e.g., carbon and nitrogen [38]. In carbon steels, the shear transformation from martensite to austenite takes

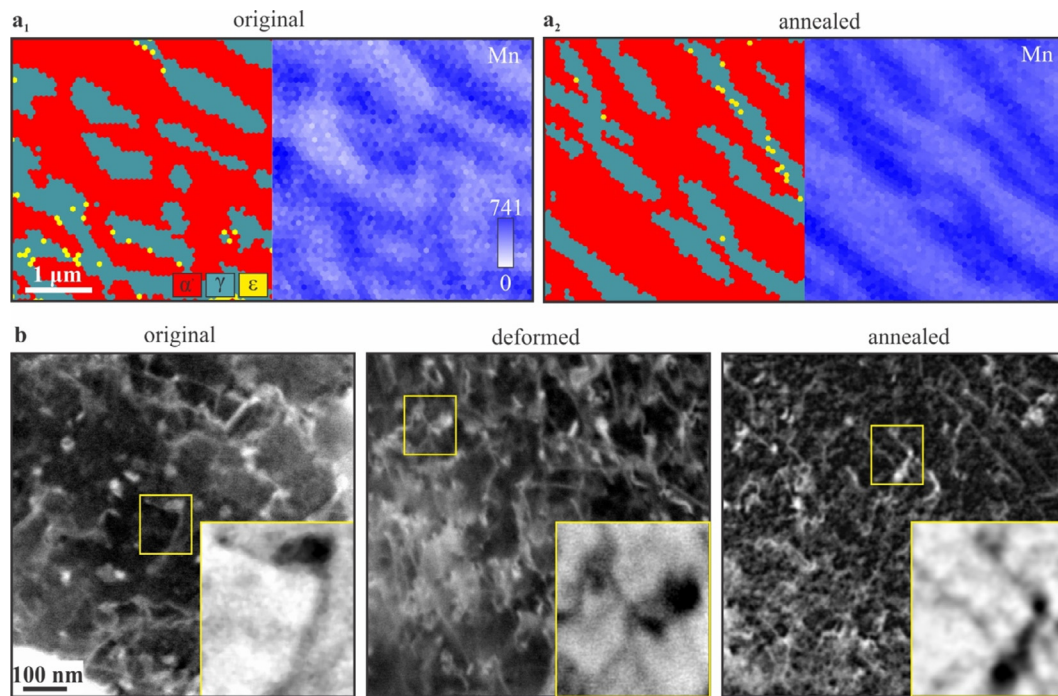


Fig. 3. (a) Mn segregation at austenite (shown here with EBSD phase and EDX Mn distribution maps) for (a₁) original and (a₂) annealed states; (b) ECCI of the martensitic matrix in the original, deformed (10% strain) and annealed states demonstrate that precipitates in martensite limit dislocation density increasing during deformation and limit dislocation recovery during annealing. Insets show how dislocations are pinned by precipitates.

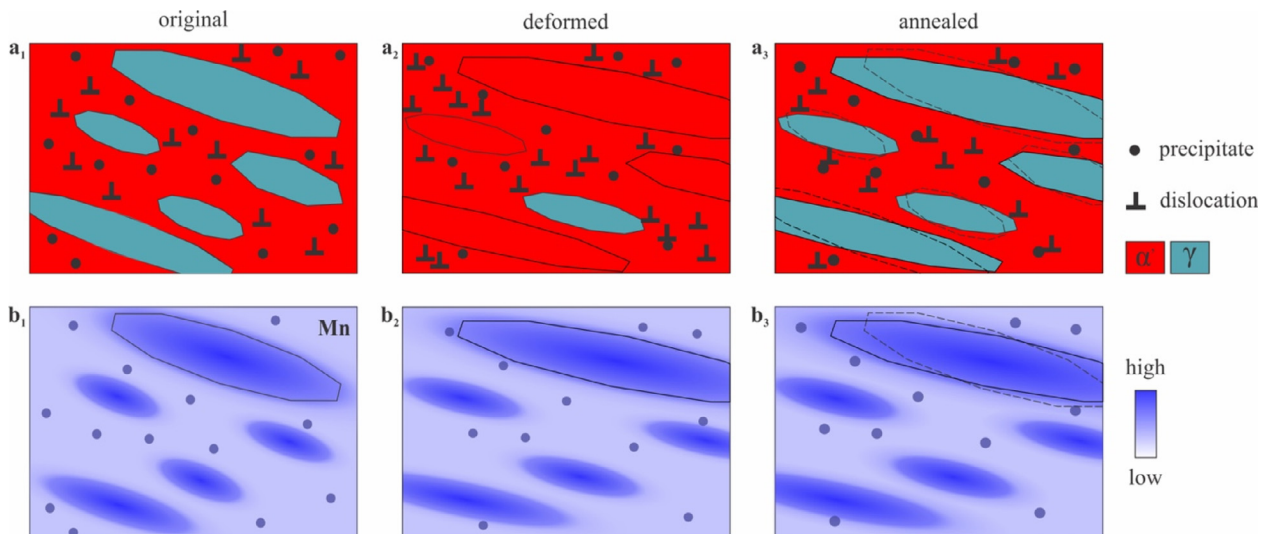


Fig. 4. Schematics of (a) phase, defects, precipitates, and (b) composition evolution during deformation and annealing.

place only at high heating rates, due to the high diffusion coefficient of carbon. When the heating rate is low, formation of cementite and ferrite is observed [44]. Here, although Mn diffusion from Mn-enriched mechanically induced martensite to Mn-depleted martensite matrix exists, there is no significant change in Mn segregation (Fig. 3a), and the nanolaminate structure is preserved even after 8 h annealing (Fig. 1a). In addition, the residual austenite (Fig. 1a) provides low energy nucleation sites for austenite re-reversion [11]. Thus, the re-reverted austenite tends to form inside original reverted austenite grains and inherits the same morphology and Mn concentration. On the other hand, two effects may be in action here that decrease the re-reverted austenite size: (i) possibility of multi-site nucleation of austenite inside a single mechanically induced martensite grain [11]; and (ii) the

increase of the elastic strain energy required for austenite formation due to the hardening of the martensite [5,45]. Smaller austenite size [23,46] and shielding effects in hardened martensite can both delay mechanically induced martensitic transformation [47,48]. To confirm this mechanism, further studies of mechanically induced martensite and reverted austenite morphology as a function of pre-strain level should be carried out.

The reported phenomena can be summarized as shown schematically in Fig. 4. TRIP-maraging steel exhibits mechanically-induced martensitic transformation during deformation (Fig. 4a₂). Given the diffusionless character of this transformation, the Mn micro-segregation from the initial reversion treatment is maintained except for minor movement caused by plastic flow (Fig. 4b₂). Martensite matrix exhibits little plasticity because of the

precipitate pinning effect. During re-reversion identical thermodynamic equilibrium conditions (same temperature and time), control the austenite fraction to return to its original state (Fig. 4a₃) and the Mn micro-segregation acts as a template for austenite re-reversion (Fig. 4b₃), promoting re-reversion kinetics. Thus, the re-reverted austenite phase mainly forms from mechanically-induced martensite but not martensite matrix, preserving the nanolaminate structure and (together with the dislocation pinning effect in martensite) limiting the scope of microstructure variation. As a result, the TRIP-maraging steel exhibits an effectively identical stress-strain response, despite multiple other changes in the microstructure due to deformation or annealing treatment.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.scriptamat.2019.12.032](https://doi.org/10.1016/j.scriptamat.2019.12.032).

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