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Effect of copper on annealing characteristics of interstitial free steels

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Abstract The effect of copper on the annealing behaviour of interstitial free (IF) steel has been investigated using thermoelectric power (TEP) and resistivity measurements. Kinetics of annealing of cold rolled copper-containing IF steel was found to be sluggish when compared with the base steels. TEP measurement revealed that copper has a negative coefficient of TEP in α-iron.

Introduction

Interstitial free (IF) steels are superformable steels (Lankford parameter, $r_m \geq 1.8$; strain hardening exponent, $n \geq 0.22$) with exceptionally low levels of carbon and nitrogen (typically, total C < 0.003 wt.% and total N < 0.004 wt.%) [1, 2]. Small amounts of 'stabilising' elements such as Ti and/or Nb are added to these steels to precipitate out the interstitials in the form of carbide, nitride, sulphide or carbosulphide thus leaving the matrix essentially interstitial free. These steels are widely used for making auto-body components. A major drawback of IF steels is their low strength (≤ 360 MPa). This has been addressed to some extent through the application of various metallurgical concepts such as solid solution strengthening (using P, Mn and Si), work hardening and strain ageing to achieve strength of about 450 MPa [3]. It is possible to achieve even higher strength (>550 MPa) in IF steels by making use of classical age hardening effect of copper in α-iron [4–6]. Thus, addition of copper to highly formable IF steels can make them stronger and dent resistant, which are desirable for better fuel-economy and improved performance of the vehicle. The high formability of IF steels would be utilised by press forming the material in the as-annealed condition when it is soft and formable, and then it can be aged to give rise to high strength. The stabilisation of interstitials by addition of Ti and/or Nb would still be required in the presence of copper, since interstitials must be removed from the solid solution to ensure the high formability [1]. The annealing behaviour of IF steels is important because it governs the development of texture in the material which in turn determines its formability [7, 8]. Accordingly, present work was undertaken to study the annealing behaviour of a new copper-alloyed interstitial free (IF-Cu) steel and compare it with that of IF steel and rephosphorised high strength IF (IF-HS) steel.

The kinetics of recrystallisation during annealing of the three steels was studied using resistivity and hardness measurements and by microstructure characterisation. In addition to these conventional techniques, a relatively novel method based on thermo electric power (TEP) measurement was also used for studying the annealing behaviour. The principle of TEP is based on the Seebeck effect and it is emerging as a powerful technique for studying various metallurgical phenomena like cold working, annealing, precipitation, measurement of solute content in solid solution etc. [9–13].

Experimental

The copper-containing IF (IF-Cu) steel was melted and cast in the form of 20 g button using IF steel and electrolytically

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pure copper charge in a tungsten inert gas (TIG) arc furnace under a protective atmosphere of pure Argon. IF and IF-HS steels were received as 4 mm thick hot rolled strips. The compositions of the three steels studied are listed in Table 1. All the alloys are essentially Ti-stabilised IF steels with a small amount of Nb. The IF and IF-HS sheets were cold rolled to 0.8 mm thick sheets, giving a reduction of 80%. The cast IF-Cu steels were cold forged and then homogenised in H_2-flow tubular furnace at 1373 K for 1 hour. The properly homogenised samples were cold rolled into 0.7 mm thick sheets, giving a reduction of 80%. The cold rolled sheets of all the three steels were annealed in a salt bath furnace at 923 K and 973 K for up to 60 min at each temperature. The homogenised samples of IF-Cu steel were subjected to aging at 773 K and 823 K.

Resistance was measured by four-terminal method inside constant temperature baths of 293 K (room temperature) and 77 K (liquid nitrogen temperature) and the values were converted to resistivity. The accuracy of resistance measurement was 99.98%. Measurements at liquid nitrogen temperature were carried to minimise the thermal effects so as to isolate the effect of composition on resistivity as per Matthiessen's rule [14].

TEP was measured on 100 mm × 7 mm × 0.8 mm strip samples with pure copper as reference material. The TEP values reported in this work are thus relative to pure copper and not absolute TEP values of the steel samples. The cold junction was kept at 293 K and a ΔT of 5 K was maintained between the hot and the cold junctions. Temperature and voltage differences both were measured with two Keithley 181 nanovoltmeters having resolution of 1 nV. The magnitude of TEP was calculated using the formula, $|S| = |\Delta V/\Delta T|$, where S is the Seebeck coefficient or simply the thermoelectric power (TEP) and ΔV is the voltage generated across the cold and hot junctions. Other details of the TEP set-up can be found elsewhere [15].

Vickers microhardness was measured at a load of 5 gf and average of 10 measurements is reported. Samples were prepared for optical microscopy following standard metallography techniques. The fraction of recrystallised grains was determined using point count method as per ASTM E112-82 standard.

Results

A series of optical microstructures shown in Figs. 1–3 reveals that while IF and IF-HS steels started to recrystallise in 10 min at 973 K, it took around 30 min for IF-Cu steel at the same temperature. The data for onset of recrystallisation for the three steels at 923 K and 973 K are summarised in Table 2. As is customary, a recrystallised volume fraction of 5% was taken to indicate the beginning

Table 1 Compositions of the investigated steels in wt.%

Steel	C	Mn	S	P	Si	Cu	Al	Ti	Nb	N
IF	0.0030	0.12	0.010	0.010	0.007	–	0.057	0.050	0.011	0.0040
IF-HS	0.0025	0.38	0.008	0.045	0.016	–	0.040	0.045	0.004	0.0047
IF-Cu	0.003	0.12	0.010	0.010	0.007	0.8	0.057	0.050	0.011	0.0040

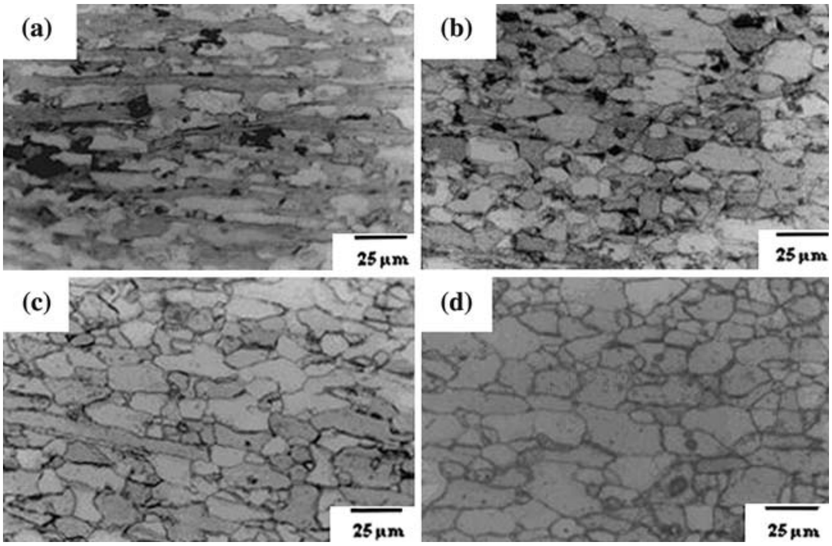

Fig. 1 Optical micrographs of IF steel annealed at 973 K for (**a**) 5, (**b**) 10, (**c**) 40, and (**d**) 60 min

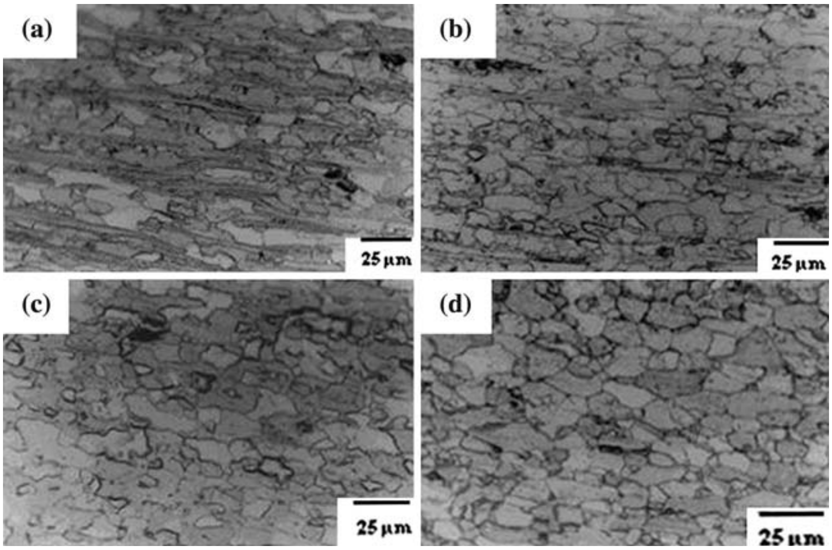

Fig. 2 Optical micrographs of IF-HS steel annealed at 973 K for (**a**) 5, (**b**) 10, (**c**) 40, and (**d**) 60 min

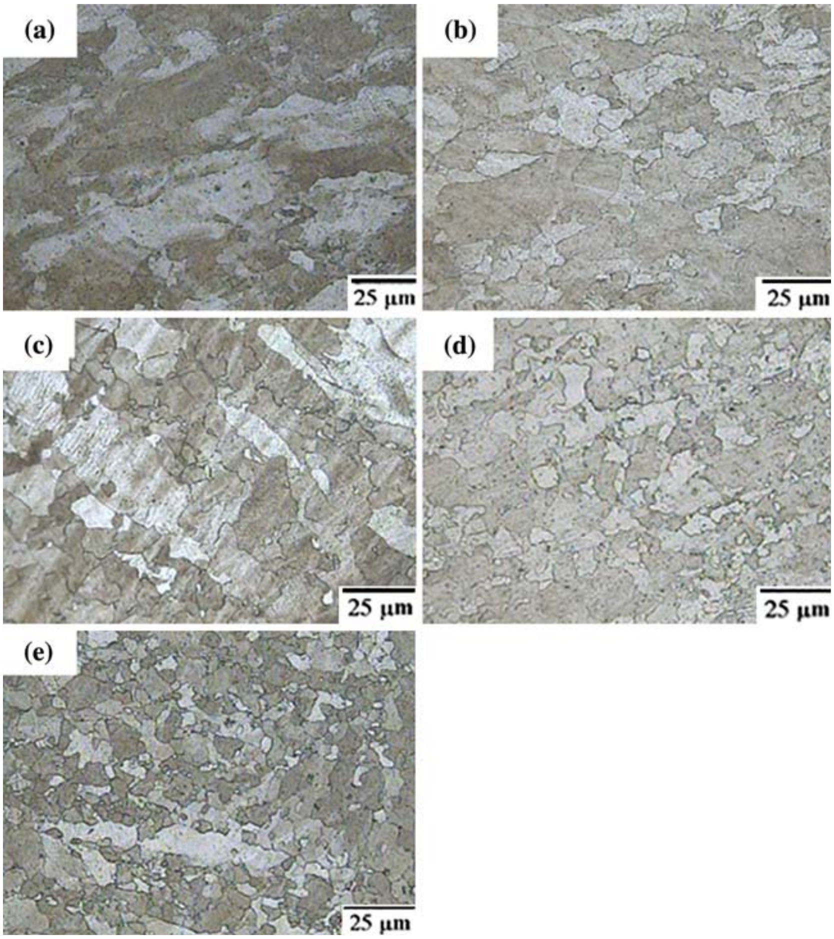

Fig. 3 Optical micrographs of IF-Cu steel annealed at 973 K for (**a**) 1, (**b**) 5, (**c**) 10, (**d**) 30, and (**e**) 60 min

of recrystallisation. The data clearly indicate an inherent sluggishness of recrystallisation kinetics in IF-Cu steel.

The microhardness, plotted in Fig. 4, showed a sharp fall within the first few minutes in all the three steels. The microhardness drop in the first 5 min of annealing ($\Delta H_{5\min}$) as a fraction of the maximum drop ($\Delta H_{\max}$) is given in Table 3. Figure 4 and Table 3 both reveal that the rate of change is very small in IF-Cu steel, confirming the findings from microstructural studies that kinetics of recrystallisation in IF-Cu steel is sluggish. Annealing at higher

Table 2 Comparison of the time for onset of recrystallisation (5% recrystallisation) as observed from microstructures

Temperature of annealing, K	Time for onset of recrystallisation, minute		
	IF	IF-HS	IF-Cu
923	40	40	>60
973	10	10	30

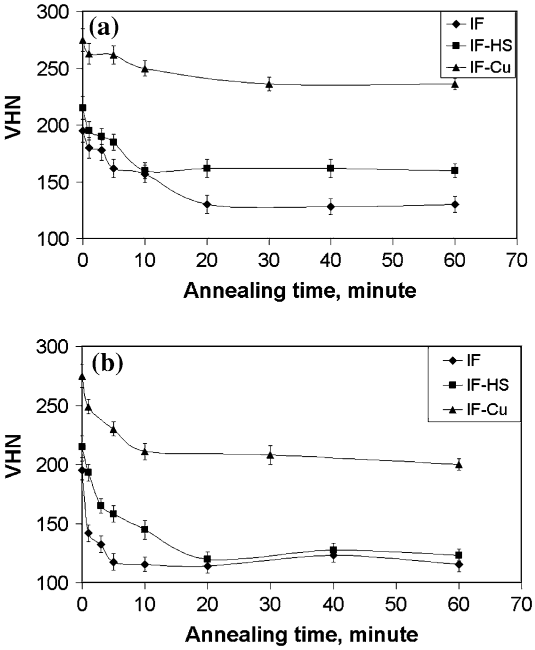

Fig. 4 Microhardness variation of the steels during annealing at (**a**) 923 K and (**b**) 973 K

Table 3 Comparison of microhardness drop in the first five minutes of annealing of the investigated steels

Temperature of annealing, K	$\Delta H_{5\mathrm{min.}}/\Delta H_{\mathrm{max.}}$ (Microhardness drop in the first 5 min of annealing ($\Delta H_{5\mathrm{min.}}$) as a fraction of maximum drop (ΔH_{max}))		
	IF	IF-HS	IF-Cu
923	56%	56%	28.5%
973	96%	88%	52%

temperature (973 K) brought about a relatively rapid and large drop in microhardness values (Fig. 4 and Table 3).

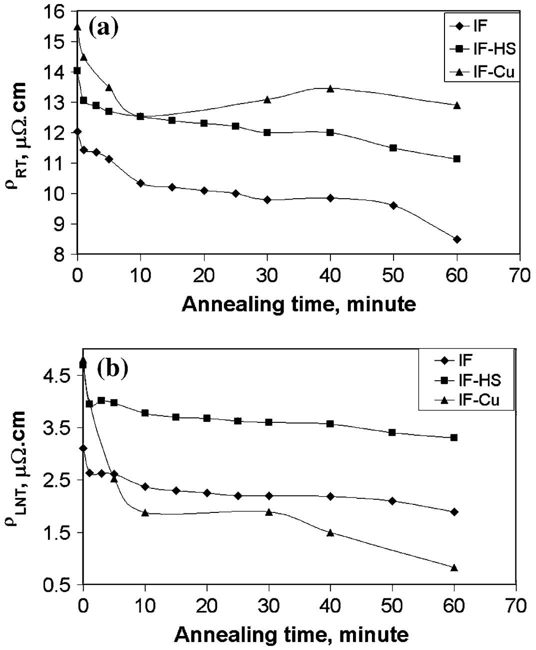

Fig. 5 Resistivity change of the steels annealed at 973 K (**a**) at 293 K and (**b**) at 77 K. ρ_{RT} and ρ_{LNT} refer to resistivity at 293 K (room temperature) and at 77 K (liquid nitrogen temperature), respectively

The variation of resistivity with time of annealing at 973 K is shown in Fig. 5. Room temperature (293 K) resistivity values of IF-Cu steel are higher than those of IF and IF-HS steels (Fig. 5a). However, when the resistivity measurements were performed at the liquid nitrogen temperature (77 K), the resistivity of IF-Cu steel was found to be lower than that of IF and IF-HS steels after 10 min of annealing (Fig. 5b). The resistivity of IF-HS steel is higher than that of IF steel. It should be noted that the resistivity measurement at liquid nitrogen temperature is more useful for monitoring the progress of annealing because the thermal effects are minimised at the liquid nitrogen temperatures; the mean free path of electrons and hence the resistivity is controlled primarily by chemical composition [14]. At the liquid nitrogen temperature, the fall in resistivity of IF-Cu steel in the early stages of annealing was sharper than in other steels. Moreover, in IF-Cu steel decrease in resistivity continued up to 60 min of annealing, whereas for IF and IF-HS steels, the resistivity values saturated after 10 min of annealing.

Figure 6 shows the change in TEP values with annealing time. While the TEP value of cold rolled IF-Cu steel is much lower than that of cold rolled IF and IF-HS steels, the TEP of IF-HS is only marginally lower than that of IF steel. In all the cases the TEP values recorded an increase as annealing progressed. In IF and IF-HS steels, the TEP attained its saturation value in 10 min of annealing at 973 K. However, in case of IF-Cu steel, TEP values showed an increasing trend even after 60 min of annealing at 973 K. Moreover, the TEP value of IF-Cu steel even after 60 min of annealing treatment at 973 K was lower than the TEP values of cold rolled IF and IF-HS steels.

In summary, at 973 K all the properties changed by the largest amount in first 10 min of annealing in IF and IF-HS steels and in 30 min in case of IF-Cu steel (Table 4). These

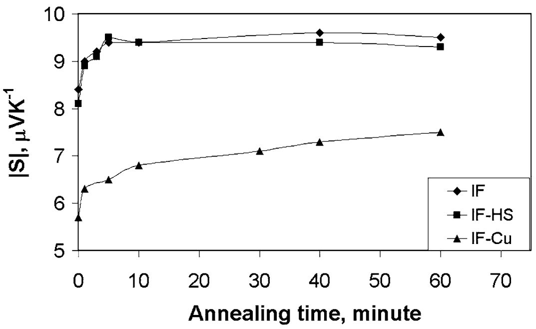

Fig. 6 Thermoelectric power, |S| variation of the steels annealed at 973 K

Table 4 Comparison of the change in measured properties during annealing at 973 K (after 10 min for IF and IF-HS steels and after 30 min for IF-Cu steel)

Properties	Change in properties as a fraction of total change, %		
	IF (10 min)	IF-HS (10 min)	IF-Cu (30 min)
Resistivity at 77 K	61	66	73
TEP	91	93	78
Microhardness	99	75	89

time periods correspond to the time for onset of recrystallisation for the respective steels, as observed from the microstructure.

Discussion

The above results show that the progress of annealing as measured by the conventional techniques (microhardness, resistivity, optical microscopy) is in good agreement with that indicated by the relatively new technique of TEP measurement. Dislocations in a metal or alloy act as the scattering sites for electrons, hindering their motion. The electrical resistivity thus decreases during recovery stage of annealing (Fig. 5) as the dislocation density decreases due to dislocation annihilation [16]. It should be noted that though resistivity changes during recovery, microstructure might not show any apparent change during this stage at the magnifications possible with optical microscope [17]. Thus at 973 K, a large drop in resistivity was observed in the first 10 min of annealing of IF-Cu steel also even though this steel did not begin to recrystallise until after 30 min (Table 2, Fig. 5).

TEP has also been reported to be very sensitive to line defects but the dependence of TEP on the dislocation density is quite different from that of resistivity [12, 18, 19]. Therefore in all the steels, TEP values increased (Fig. 6) while resistivity decreased as annealing progressed at 973 K. Precipitation of copper is expected to take place in IF-Cu steel during annealing [5, 6, 20, 21] and this should also influence the measured TEP values [11, 13]. In case of IF-Cu steel, both resistivity and TEP values continued to change even after longer annealing times indicating an inherent sluggishness of the progress of recovery. This can be attributed to the classical solute drag effect of copper and also to Zener drag of expected copper precipitates, which tend to pin down the dislocations [22–24]. Relatively gradual drop in microhardness (Fig. 4) and the longer time required for onset of recrystallisation (Table 2) in IF-Cu steel corroborate this.

The presence of phosphorus in IF-HS steel causes lattice distortion [25] and thus provides scattering centres for electrons. Therefore, the resistivity of IF-HS steel is higher than that of IF steel at both the measurement temperatures (Fig. 5). The room temperature (293 K) resistivity of IF-Cu is higher than that of IF and IF-HS steels at all stages of annealing (Fig. 5a). However, at the liquid nitrogen temperature (77 K) IF-Cu steel has the lowest resistivity after 10 min of annealing (Fig. 5b). Copper is known to cause precipitation hardening in iron-based systems [5, 20, 21]. A variety of experimental techniques like field ion microscopy (FIM), high resolution transmission microscopy (HRTEM), and X-ray absorption techniques such as EXAFS and XANES have been used to establish the precipitation sequence in Fe-Cu system which is given below [21, 26–31]:

$$\text{Supersaturated solid solution} \rightarrow \text{bcc Cu clusters} \rightarrow \text{9R-Cu} \rightarrow \text{3R-Cu} \rightarrow \varepsilon\text{-Cu(FCC)}.$$

These measurements indicate that in the peak aged condition copper is in the form of bcc clusters in the size ranges of 3–4 nm that form at 773–823 K [5]. However, in the IF-Cu steel in the present work, over aged precipitates of copper are expected to form during annealing at a relatively high temperature of 973 K [20]. These precipitates are in addition to other precipitates of Ti (TiC, $Ti_4C_2S_2$ etc.) that from in Ti-stabilised IF steels [32]. It is possible that the temperature coefficient of resistivity of this material with copper precipitates is quite different from that of IF and IF-HS steel. This difference in the temperature coefficient of resistivity may be responsible for the difference in the relative resistivities of IF-Cu steel on the one hand and IF and IF-HS steel on the other when measurements were made at 293 K and 77 K (Fig. 5). It is pertinent to note in this context that even in the cold rolled condition (when copper is completely in solid solution), the temperature coefficient of resistivity of IF-Cu steel appears to be

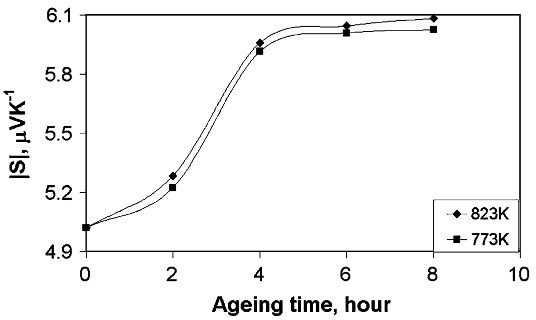

Fig. 7 Thermoelectric power, |S| variation of IF-Cu steel aged at 773 and 823 K

higher than the other two steels. At 293 K, the resistivity of cold worked IF-Cu steel is significantly higher than that of IF-HS steel in the cold worked condition (annealing time = 0), but at 77 K, both the steels have similar resistivity values. This indicates a relatively large drop in resistivity of IF-Cu steels when the temperature decreases from 293 K to 77 K. Precipitation of copper during annealing of IF-Cu steel perhaps further raised the temperature coefficient of resistivity of this material leading to the behaviour observed in Fig. 5(a, b). Though a plausible explanation has been presented here for these observations on resistivity of the three steels at different temperatures, further detailed study is clearly required to understand the phenomenon better.

The TEP values of IF-Cu steel are much lower than those of IF and IF-HS steels in all the conditions studied (Fig. 6). This indicates that like most other alloying elements [33], copper in solution in α-iron has a negative coefficient of TEP. The increase in TEP on aging the solutionised IF-Cu steel (Fig. 7) confirms this [15].

The mechanism of annealing in IF steels has been the subject matter of debate in literature reports [34, 35]. In the present work, the microhardness drop in the three steels is primarily due to recovery. This is in contrast to the conventional annealing behaviour where hardness or strength falls mainly in the recrystallisation stage of annealing. Sharp change in resistivity and TEP values in the early stage of annealing at 973 K confirm this.

Conclusion

- Thermoelectric power and resistivity techniques appear to be useful tools in characterising the annealing behaviour of IF steels.
- Annealing kinetics of IF steel containing 0.8 wt.% copper is slower than IF and IF-HS steels. 923 K is too low a temperature for annealing the copper-containing IF steels.
- The hardness drop during annealing of IF steels is mainly due to recovery rather than due to recrystallisation.
- The coefficient of thermoelectric power of copper in solution in α-iron is negative.

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