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Structure-Property Correlation of Two Cu-Bearing High-Strength Low-Alloy Steels

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Structure and mechanical properties of two copper bearing high-strength low-alloy steels (HSLA)—one similar to HSLA 80 and the other to HSLA 100—are studied in different aging conditions. Elemental copper precipitates of nanometer size have been found to play an important role in the formation of different types of microstructures and in enhancing the strength and toughness of the alloys. Other alloying elements such as Ti, Nb, and V result in fine precipitates of carbides and nitrides, which improve the mechanical strength.

Keywords aging, HSLA steel, toughness

1. Introduction

The constructional materials used in ship-hull fabrication and other critical applications have traditionally been heat-treated low-alloy steels. These quenched and tempered steels derive their strength from their carbon content and hardenability from the alloying elements. Although they possess adequate base material yield strength and toughness, they exhibit poor weldability due both to high carbon content and high carbon equivalent.[1] The microstructural changes occurring in the heat-affected zone (HAZ) during welding increase hardness and reduce toughness resulting in an increased susceptibility to brittle fracture and hydrogen-assisted cracking.[2] Control of preheat and interpass temperatures to prevent HAZ cracking, and also use of a low heat input to maintain weld strength, results in significantly higher fabrication costs in comparison to other structural steels. In order to minimize welding costs, alternative steels with improved response to the weld thermal cycle had to be developed. The family of high-strength low-alloy (HSLA) steels with copper addition came into being as a result of this search.

The alloy design philosophy of the new steels includes a reduction in carbon content, which improves toughness and weldability. Strengthening results from a highly dislocated, aged martensite and the precipitation of copper particles.[1] The important steels in this category are HSLA 80 and HSLA 100, which have been intended as more economically weldable replacements of the HY-80 and HY-100 steels widely used earlier. Both HSLA 80 and HSLA 100 have been used during the last 10 to 15 years in offshore platforms and naval constructions.[3] Both steels are insensitive to hydrogen-assisted cracking during welding, owing to their low carbon contents, and, while HSLA 80 can be welded without preheat, the preheat requirement for HSLA 100 is much less than for HY-100. Additionally, the HSLA steels can be processed and heat treated to provide several strength and toughness combinations over a wide range of plate thicknesses.[1]

The present investigation was undertaken as part of a study of HSLA steels under an Indo-U.S. program. Two such steels, corresponding to HSLA 80 and HSLA 100 and designated as GPQ and GRV, respectively, were provided by the Naval Research Laboratory (Washington DC) in the form of plates of thickness 20 and 25 mm, respectively. An attempt has been made to study the structure formed during aging at various temperatures and to evaluate the effect of heat treatment on the mechanical properties.

2. Experimental

The chemical compositions of the two alloys, GPQ and GRV, are given in Table 1. Microstructural studies were carried out on specimens of size 1 cm^2 cut out from both the materials in the hot rolled and heat-treatedconditions. The heat treatment given is as follows:

- solutionizing for 1 h at the austenitizing temperature of 900 °C,
- water quenching to room temperature, and
- aging at different temperatures starting from 250 to 500 °C in steps of 50 °C for 1 h followed by air cooling to room temperature.

Microstructural Studies. Polished and etched specimens in all conditions of heat treatments were observed under optical microscopy. Picral with the composition of picric acid 5 g, HCL 5 mL, and methanol 50 mL was used to etch the specimens. Thin foils for transmission electron microscopy were prepared using 95% acetic acid plus 5% perchloric acid electrolyte. Identification of different phases and precipitates was carried out with energy-dispersive x-ray analysis (EDAX).

Tension and compression tests were carried out using a servohydraulic universal testing machine of 10 T capacity. Some specimens were given compressive and tensile prestraining of about 2, 4, and 6% and tested for their stress-strain behavior in compression and tension. Hardness tests were carried out using a Vicker's hardness tester. Charpy impact toughness tests

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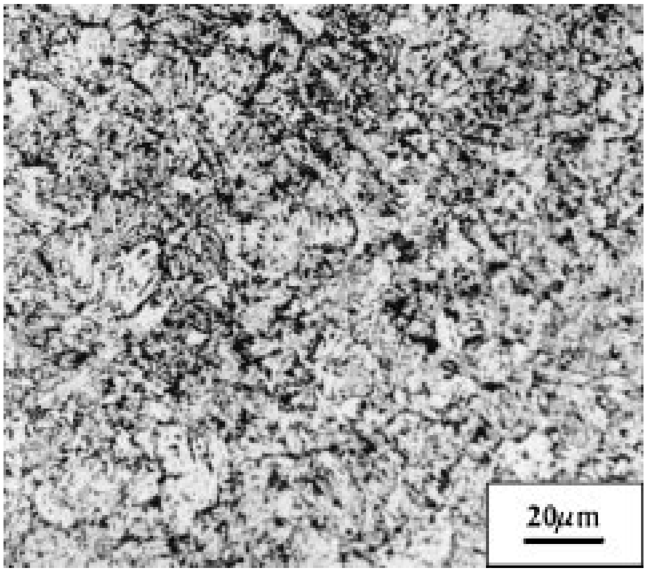


Fig. 1 Microstructure of solutionized and water-quenched sample of GPQ

Table 1 Chemical composition of GPQ and GRV HSLA steels (in wt.%)

Element	GPQ	HSLA 80	GRV	HSLA 100
C	0.052	0.06	0.048	0.06
Si	0.33	0.40	0.286	0.40
Mn	0.984	0.4–0.7	0.861	0.75–1.15
Ni	1.790	0.7–1.0	3.46	3.35–3.65
Cu	1.0	1.0–1.3	1.36	1.45–1.75
Cr	0.615	0.6–0.9	0.768	0.45–0.75
Mo	0.52	0.15–0.25	0.665	0.55–0.65
V	0.007	0.3	0.011	0.03
Co	0.006	…	0.016	…
Ti	0.01	0.02	0.01	0.02
Nb	0.03	0.02–0.06	0.033	0.02–0.06
P	0.01	0.02	0.01	0.02
S	0.002	0.006	0.002	0.006

were carried out with the standard charpy specimens. The effect of heat treatment and aging temperature on toughness was investigated.

3. Results and Discussion

3.1 Carbon Equivalent

The alloys GPQ and GRV are designed to be similar to HSLA 80 and HSLA 100, respectively. However, the nickel (1.8%) and molybdenum (0.52%) in GPQ are higher than specified for HSLA 80, while the amount of copper is slightly lower. The steel GRV is quite similar in composition to HSLA 100.

The carbon contents in both the steels investigated are low, and the carbon equivalents, CE, based on the International Institute of Welding formula

$$\%CE = C + Mn/6 + (Cr + Mo + V)/5 + (Ni + Cu)/15$$

are 0.631% for GPQ and 0.802% for GRV. These fall within the ranges for HSLA 80 (0.462 to 0.633%) and HSLA 100 (0.777 to 0.964%). Although the carbon equivalents are high, the weldability is still very good because of the low carbon levels.

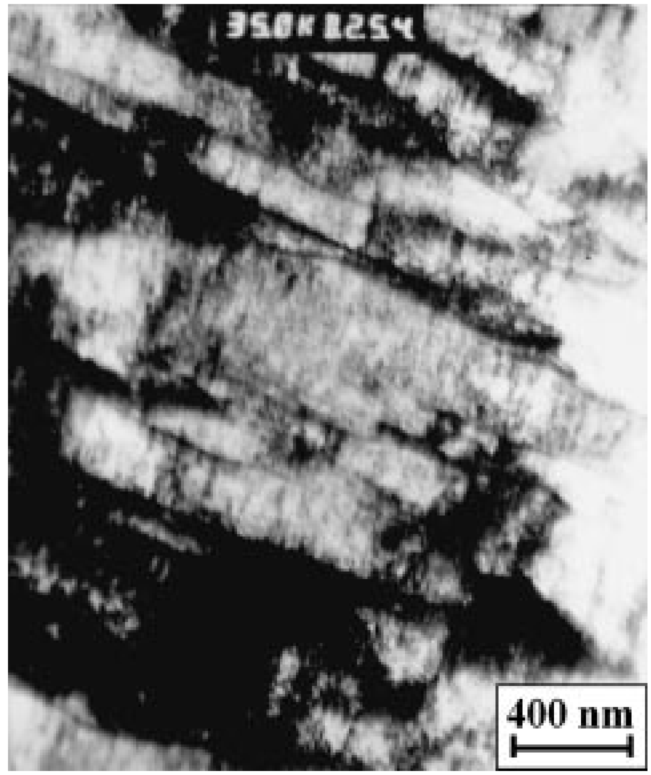


Fig. 2 TEM of heat-treated GPQ sample (900 °C solutionized/WQ)

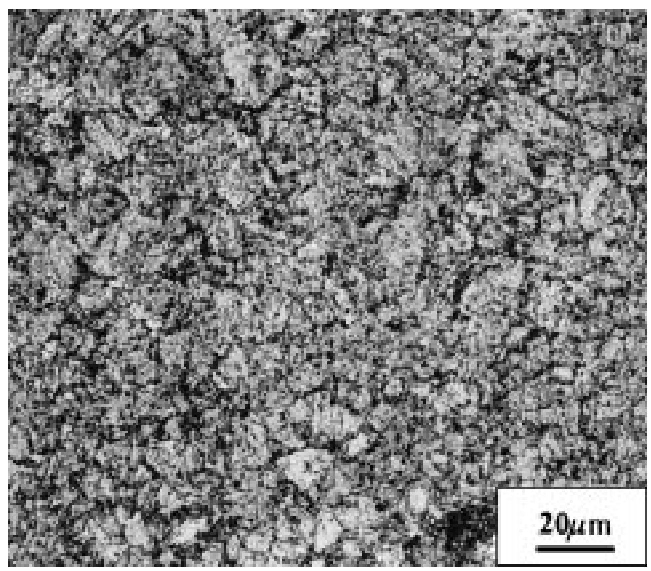


Fig. 3 Microstructure of solutionized and water-quenched sample of GRV

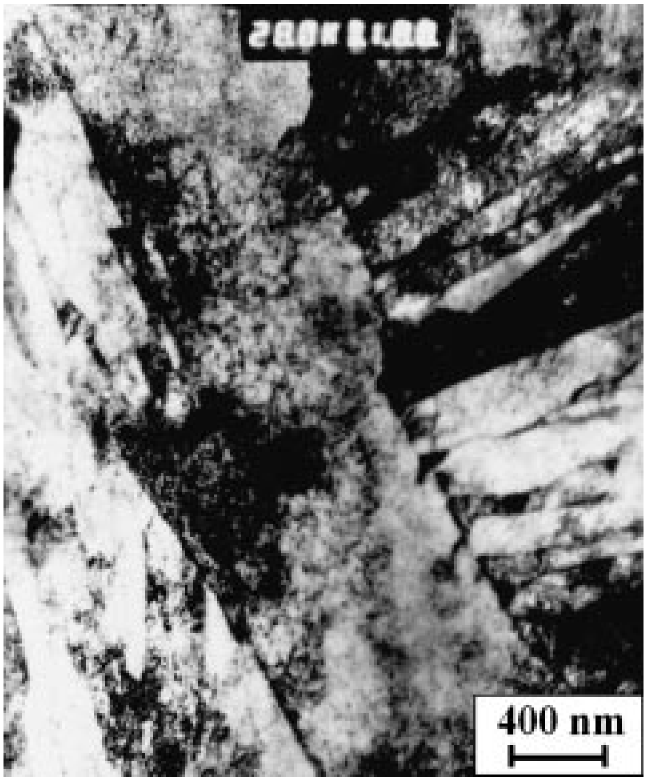


Fig. 4 TEM of heat-treated GRV sample (900 °C solutionized/WQ)

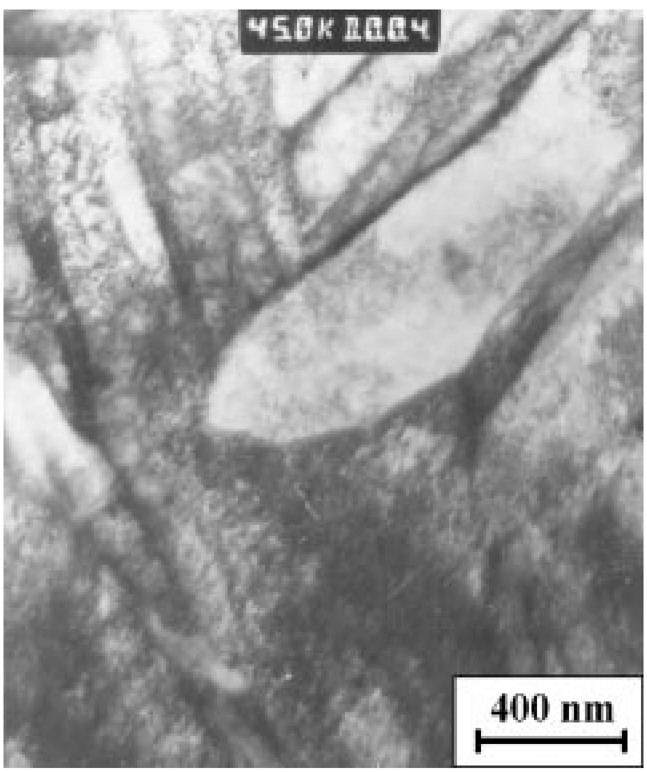


Fig. 5 TEM of heat-treated GPQ sample (900 °C 1 h/WQ/aged at 250 °C)

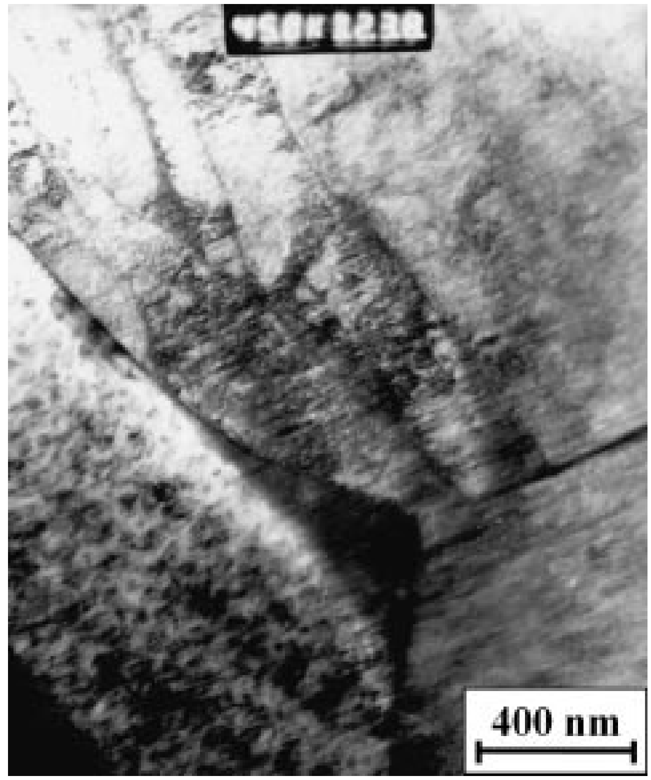


Fig. 6 TEM of heat-treated GPQ sample (900 °C 1 h/WQ/aged at 300 °C)

3.2 Microstructure

The microstructure of a specimen from the GPQ alloy after solution treatment at 900 °C and water quenching is shown in Fig. 1. The structure is martensitic and was found to exhibit a hardness of 350 VHN. The transmission electron micrograph (Fig. 2) shows laths of martensite several microns long and ten microns wide. The laths are heavily dislocated and a small amount of retained austenite is also present between some of the laths. A martensitic structure composed of dislocated laths is also observed in the solution-treated and water-quenched specimen from the GRV alloy (Fig. 3 and 4).

The microstructure of low carbon, Cu-bearing steels, on quenching from the austenitic condition, will essentially consist of martensite supersaturated with Cu and other alloying elements. The low carbon content results in a lath morphology with a high dislocation density. The presence of a greater amount of Ni in the GPQ alloy (over HSLA 80) has apparently contributed to the occurrence of some retained austenite. The precipitation reactions in Cu-containing steels have been studied by several investigators.[1,4] Initially, Cu-rich clusters with bcc structure are formed, which later transform to incoherent spherical η-phase particles with an fcc lattice; these particles grow subsequently to form rodlike precipitates at high aging temperatures. Peak strengthening usually occurs before the precipitates become incoherent and produce sufficient diffraction contrast for detection in the electron microscope. The size of the copper particles at peak hardening has been estimated to be as low as 2 to 4 nm.[4] Apart from copper precipitates, a secondary precipitate of importance is Nb(C, N). These are also fine

Fig. 7 TEM of heat-treated FPQ sample (900 °C 1 h/WQ/aged at 350 °C)

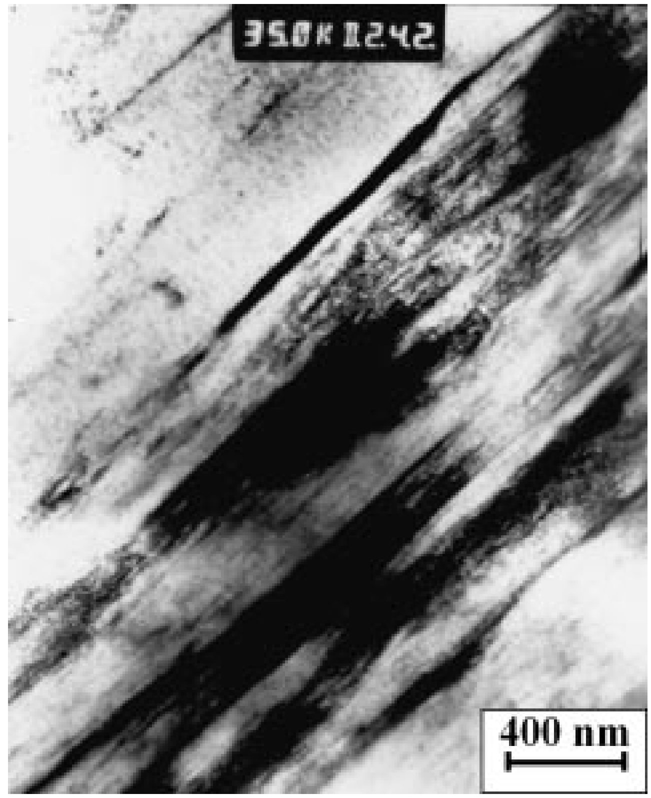


Fig. 8 TEM of heat-treated GPQ sample (900 °C 1 h/WQ/aged at 400 °C)

(6 to 10 nm), pin the austenite grain boundaries, and reduce grain size.

The TEM micrographs of GPQ specimens aged in the temperature range of 250 to 500 °C (for 1 h at each temperature) are reproduced in Fig. 5 to 11. The high dislocation density characterizing the as-quenched material is seen to persist even at the higher temperatures of aging. Some precipitation along the prior-austenite grain boundary is noticeable in the specimen aged at 300 °C (Fig. 6). The EDAX analysis showed these to be niobium rich (Nb = 43.3%), but it is believed that these precipitates, which are presumably Nb carbonitride, had already formed during the prior thermomechanical processing.

Precipitation of copper is noticeable only at the higher aging temperatures. The EDAX analysis of the specimen aged at 400 °C showed a copper content of 40.6% for a region containing the precipitates. Some evidence of recovery and recrystallization of the lath structure was also observed as the aging temperature was raised (*e.g.*, Fig. 7 and 9).

The TEM micrographs of the GRV specimens aged at different temperatures are shown in Fig. 12 to 17. The precipitation processes occurring in this alloy are similar to those in GPQ but appear to be more intense (*e.g.*, Fig. 13 to 15).

From EDAX analysis, copper precipitation could be detected even at an aging temperature of 350 °C.

3.3 Mechanical Properties

Hardness. The variation of Vicker's hardness with aging temperature is shown in Fig. 18 and 19 for GPQ and GRV

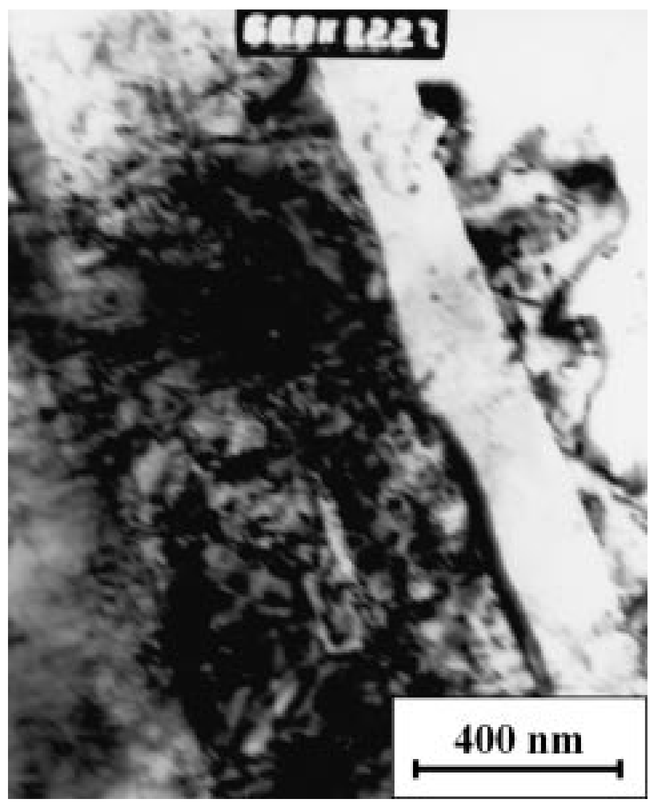


Fig. 9 TEM of heat-treated GPQ sample (900 °C 1 h/WQ/aged at 450 °C)

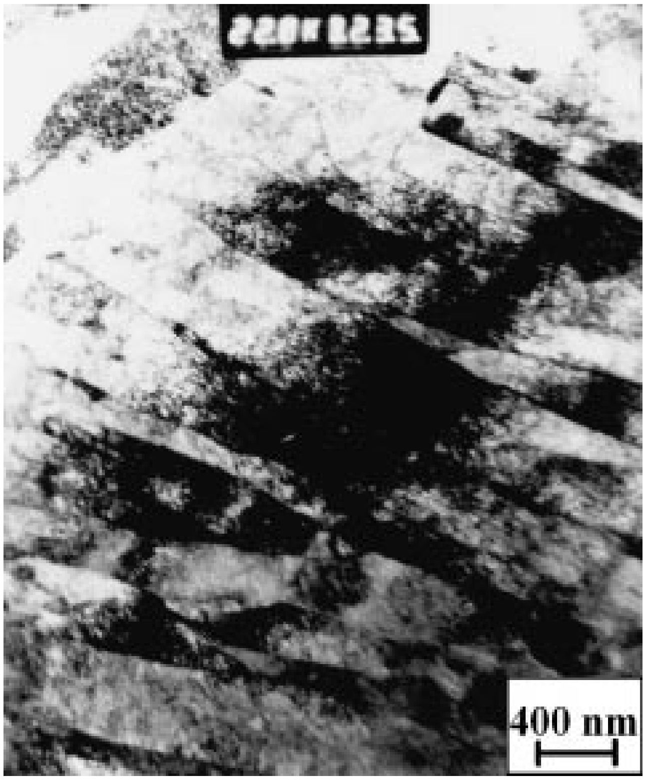


Fig. 10 TEM of heat-treated GPQ sample (900 °C 1 h/WQ/aged at 500 °C)

steels, respectively. It can be seen that aging in the temperature range of 250 to 350 °C gave the maximum hardness values of about 360 to 370 HVN in the case of GPQ. In the case of GRV, the maximum hardness is obtained at the aging temperature of 250 °C. Increasing the aging temperature decreases the hardness. So, an aging temperature of 250 °C for 1 h has been used in the subsequent investigations of stress-strain behavior.

Stress-Strain Behavior: GPQ Alloy. Figures 20(a) and (b) show the tensile stress-strain behavior of GPQ in the as received and heat-treated (austenitized at 900 °C, water quenched (WQ), and aged at 250 °C) conditions. In the as-received condition, the yield stress is 620 MPa and heat treatment increases the yield stress to 850 MPa. It can also be noted that strain hardening is not very much pronounced in the as-received material, whereas with heat treatment, strain hardening increases. Thus, the ultimate strength of the as-received material is 650 MPa and that of the heat-treated material is increased to 950 MPa. However, the fracture strain, which is 20.6% for as-received material, is reduced to 12% on heat treatment.

Figures 21(a) and (b) show the effect of prestraining on 0.2% yield stress in compression and in tension. In the case of compression loading, prestraining increases the yield stress for both as-received and heat-treated materials, whereas in the case of tension prestraining, as-received material does not show much increase in the yield stress, as the strain hardening is very low in this condition. Even in the case of the heat-treated condition, the increase in strength is observed up to 2% prestrain. Afterward, there is not much increase in the yield stress.

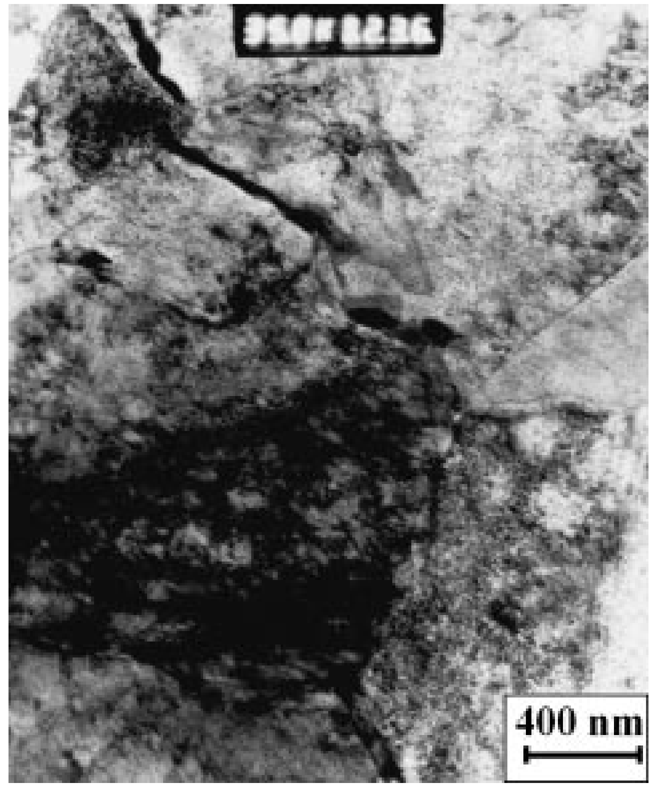


Fig. 11 TEM of heat-treated GPQ sample (900 °C 1 h/WQ/aged at 500 °C)

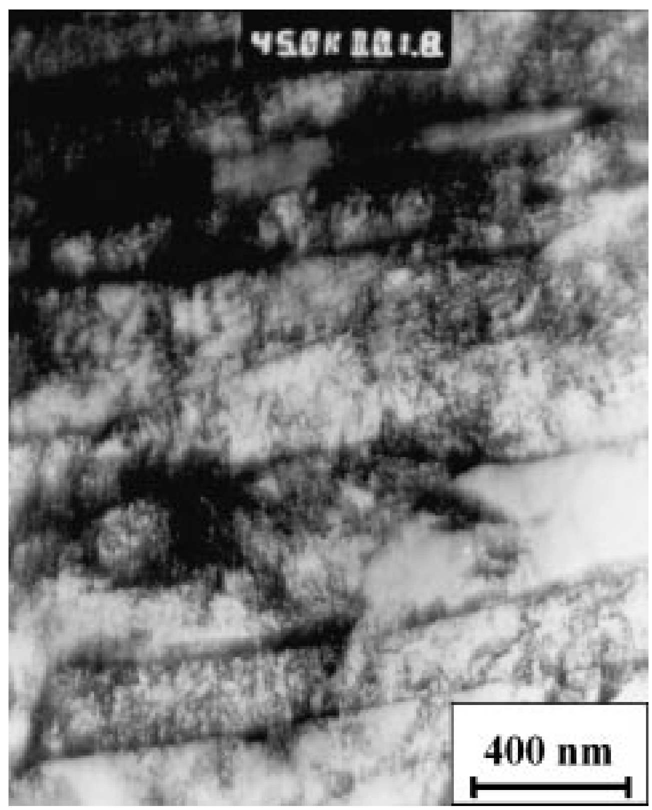


Fig. 12 TEM of heat-treated GRV sample (900 °C 1 h/WQ/aged at 250 °C)

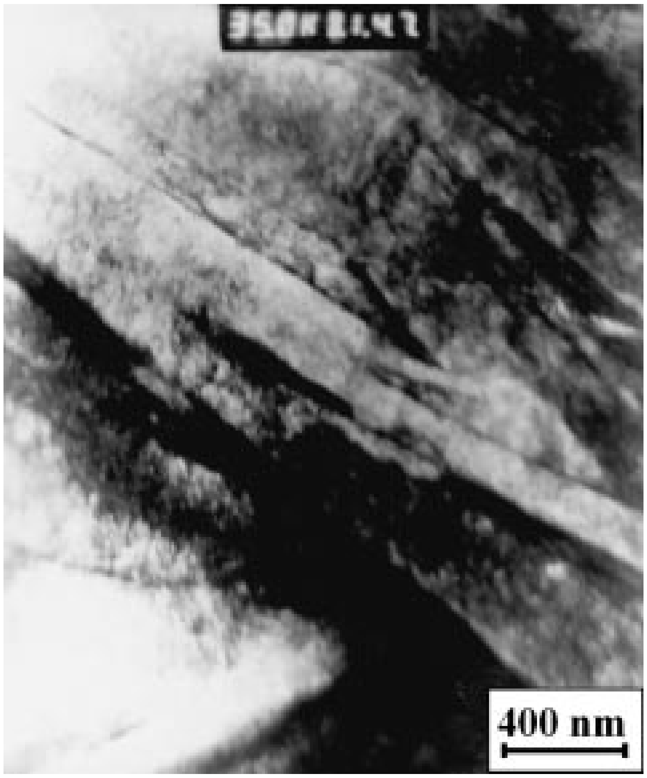


Fig. 13 TEM of heat-treated GRV sample (900 °C 1 h/WQ/aged at 300 °C)

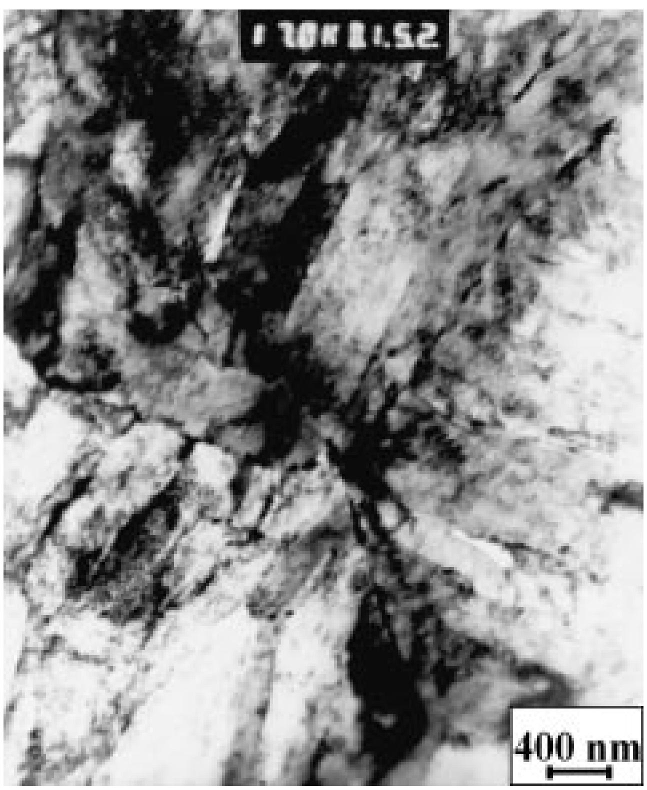


Fig. 14 TEM of heat-treated GRV sample (900 °C 1 h/WQ/aged at 350 °C)

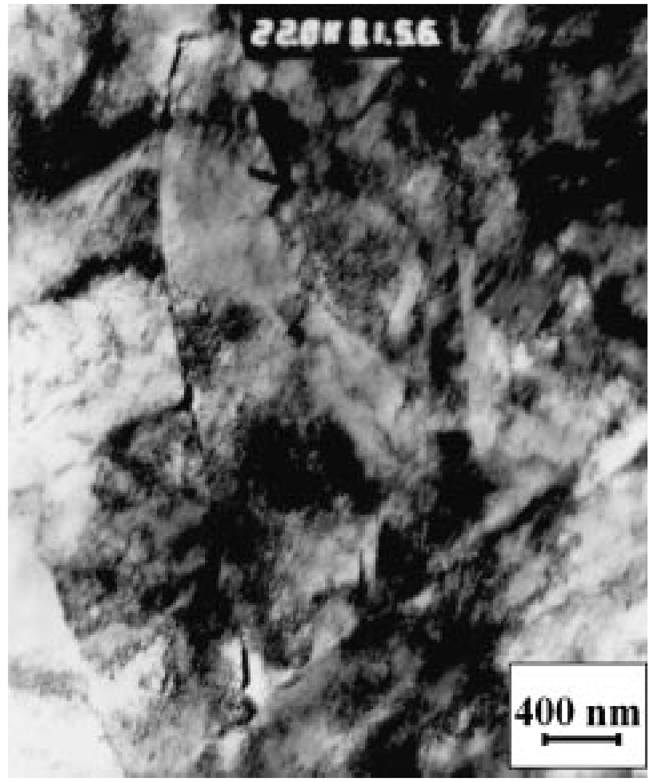


Fig. 15 TEM of heat-treated GRV sample (900 °C 1 h/WQ/aged at 400 °C)

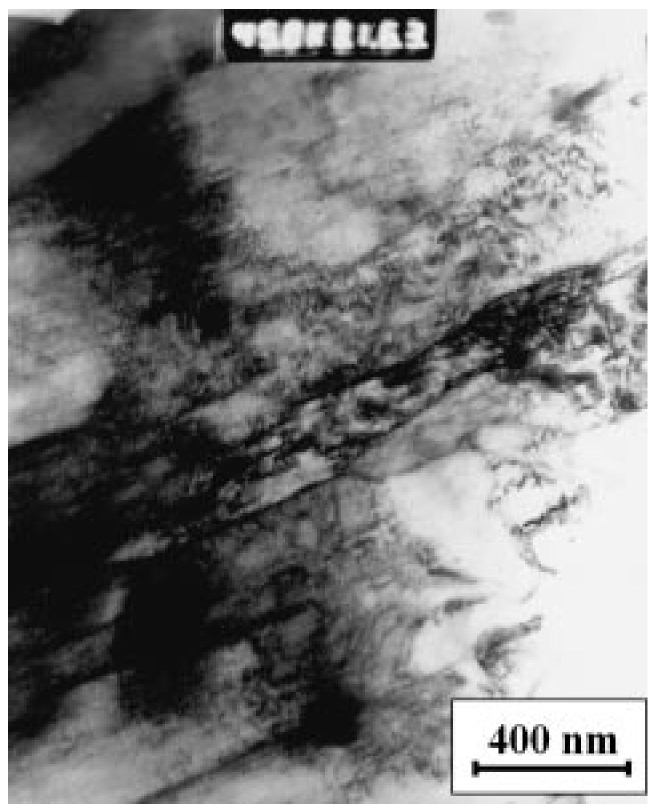


Fig. 16 TEM of heat-treated GRV sample (900 °C 1 h/WQ/aged at 450 °C)

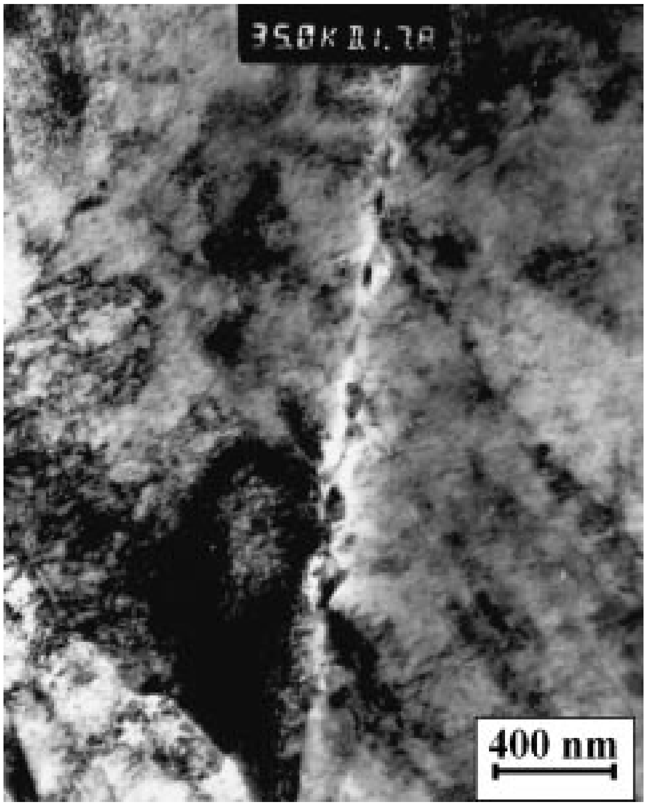


Fig. 17 TEM of heat-treated GRV sample (900 °C 1 h/WQ/aged at 500 °C)

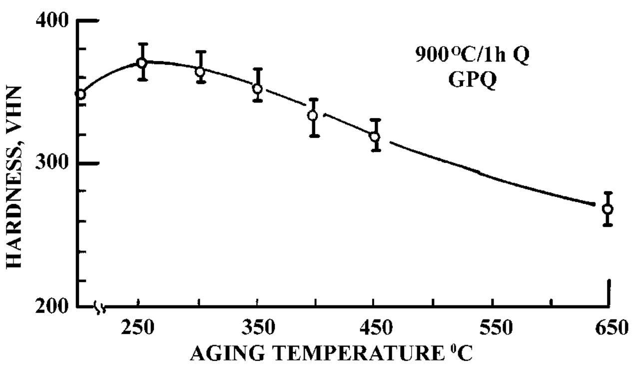


Fig. 18 Variation of Vicker's hardness with aging temperature (GPQ)

GRV Alloy. Figures 22(a) and (b) show a typical stress strain behavior of as-received and heat-treated GRV material in tension with 4% tensile prestrain. The yield strength in tension is 870 MPa for the as-received material. The ultimate tensile strength (UTS) is 930 MPa and the strain corresponding to the UTS is 4 to 5% only. The strain hardening is very low and the fracture strain is around 10%. Since beyond 5 to 6% of plastic strain the stress starts decreasing, prestraining beyond these values is difficult in normal tensile type prestraining. Prestraining increases the yield strength of the alloy. The heat-treated alloy shows a yield strength of 940 MPa and a UTS of 1100 MPa. The fracture strain is 8 to 8.5%.

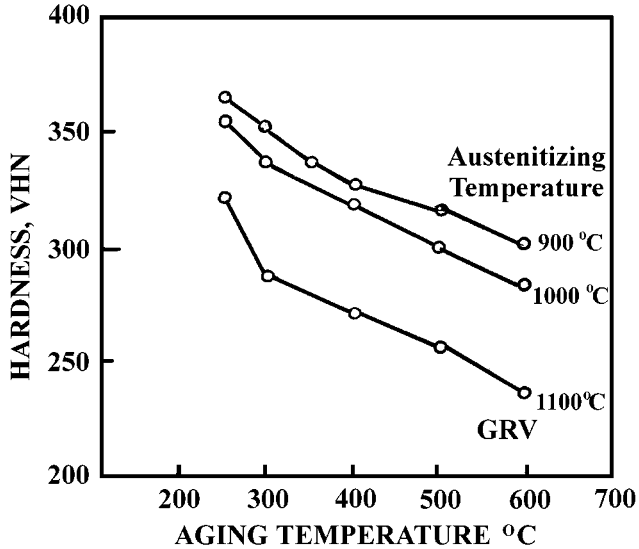


Fig. 19 Variation of Vicker's hardness with aging temperature (GRV)

Variation of yield strength with prestraining is shown in Figs. 23(a) and (b) in compression and in tension, respectively. In compression, prestraining shows a continuous increase in the yield stress up to 6% in both as-received and heat-treated conditions. In the case of tensile prestraining, it can be seen that, though the yield strength increases with prestraining, beyond 4% in the as-received condition and 2% in the heat-treated condition, the value of the yield stress decreases.

Impact Toughness. The variation of charpy impact energy with aging temperature of the GPQ steel is shown in Fig. 24. The impact energy is high in the range of 160 J for the as-received material. Solutionizing and aging the alloy in the range of 250 to 400 °C improves the impact toughness only marginally to 170 J. However, increasing the aging temperature to 500 °C gives a clear increase to 190 to 195 J. In the impact toughness specimens, the fracture surface is not plane and perpendicular to the sides, but is curved, indicating resistance to fracture. Shear lip type of fracture is observed in all cases.

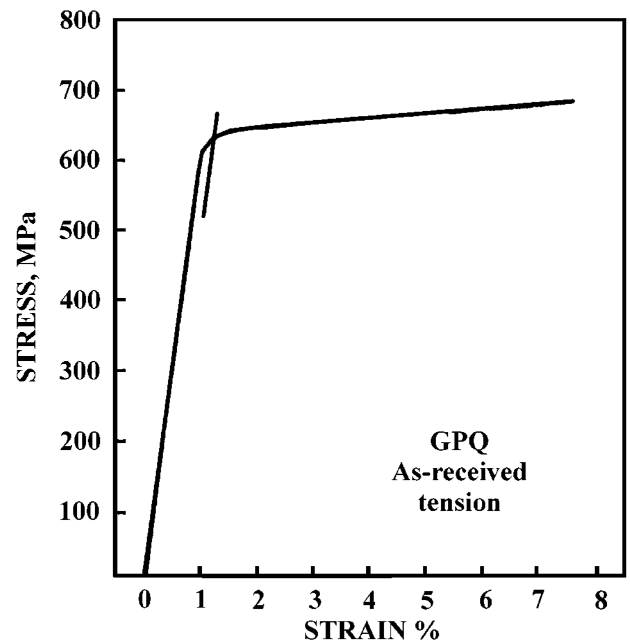
The fracture toughness tests per ASTM E 399 could not be carried out. However, the fracture toughness K_{Ic} has been calculated using the relation

$$(K_{Ic})^2 = 5 \text{ YS } (\text{CVN} - \text{YS}/20)$$

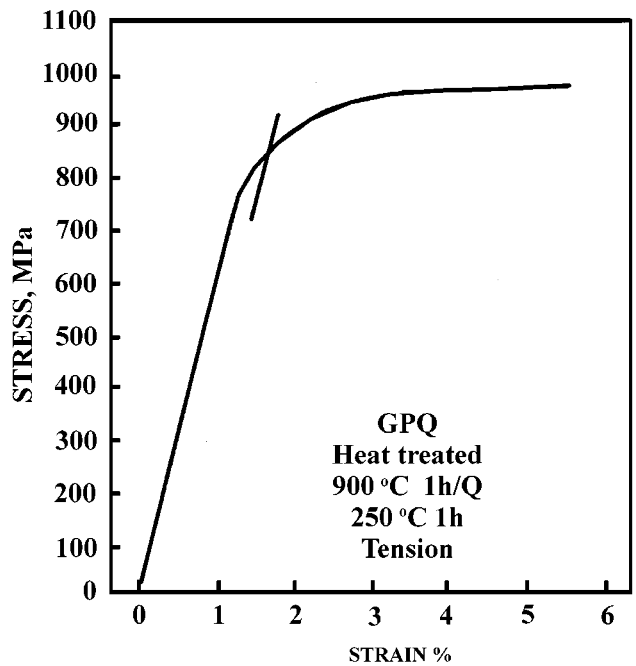
where K_{Ic} is in ksi$\sqrt{\text{in.}}$, YS is the yield stress in ksi, and CVN is the impact energy in ft. lbs.

For the as-received GPQ, the YS is 620 MPa and CVN is 158 J. Using these values, we get the fracture toughness of the as-received GPQ as 240 MPa$\sqrt{\text{m}}$. For the heat-treated alloy, YS is 850 MPa and CVN is 160 J. Thus, we get the notional value of the fracture toughness $K_{Ic} = 290$ MPa$\sqrt{\text{m}}$. These values of K_{Ic} calculated from the charpy impact values show high K_{Ic} for the material. It is possible to get such high fracture toughness values for the alloy investigated because of the microalloying elements it contains and the thermomechanical treatment given to it.

Figure 25 shows the relation between the charpy impact energy and the aging temperature of the GRV alloy. The as-



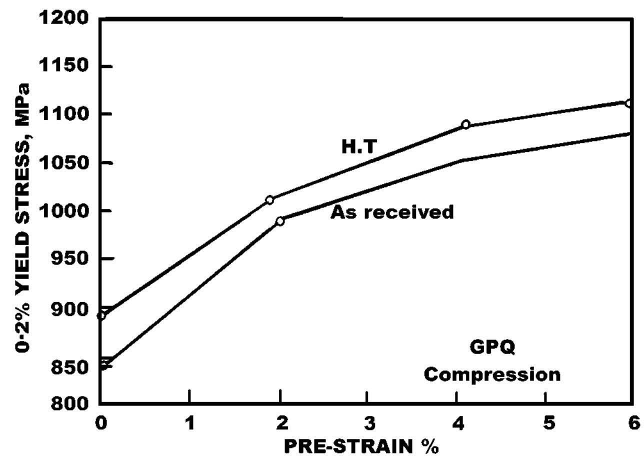
(a)



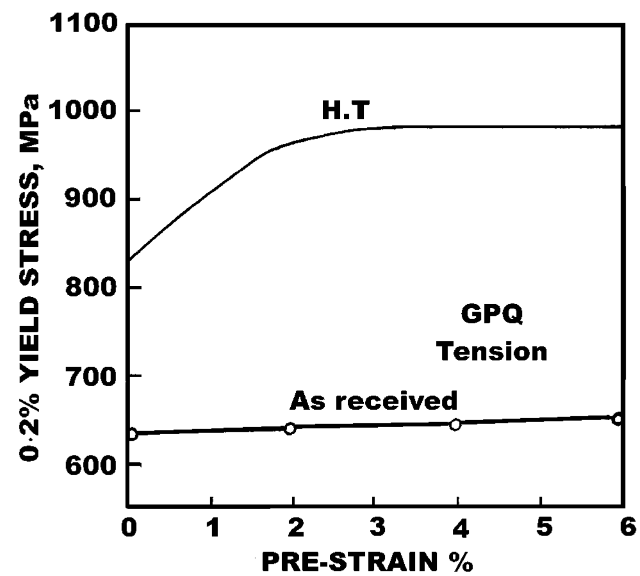
(b)

Fig. 20 **(a)** Tensile stress-strain relation of GPQ (as-received). **(b)** Tensile stress-strain relation of GPQ heat treated (900 °C 1 h/WQ/ aged at 250 °C)

received alloy shows the highest toughness in the range of 190 to 195 J. The alloy is very tough and shear lip type of fracture is observed. Heat treatment in the range of 250 to 400 °C has reduced the charpy toughness to 140 to 145 J. However, increasing the aging temperature to 500 °C increases the toughness to 170 J. The fracture toughness K_{Ic} of the as-received material is around 290 $\text{MPa}\sqrt{\text{m}}$ and that of the heat-treated materials is 260 $\text{MPa}\sqrt{\text{m}}$.



(a)



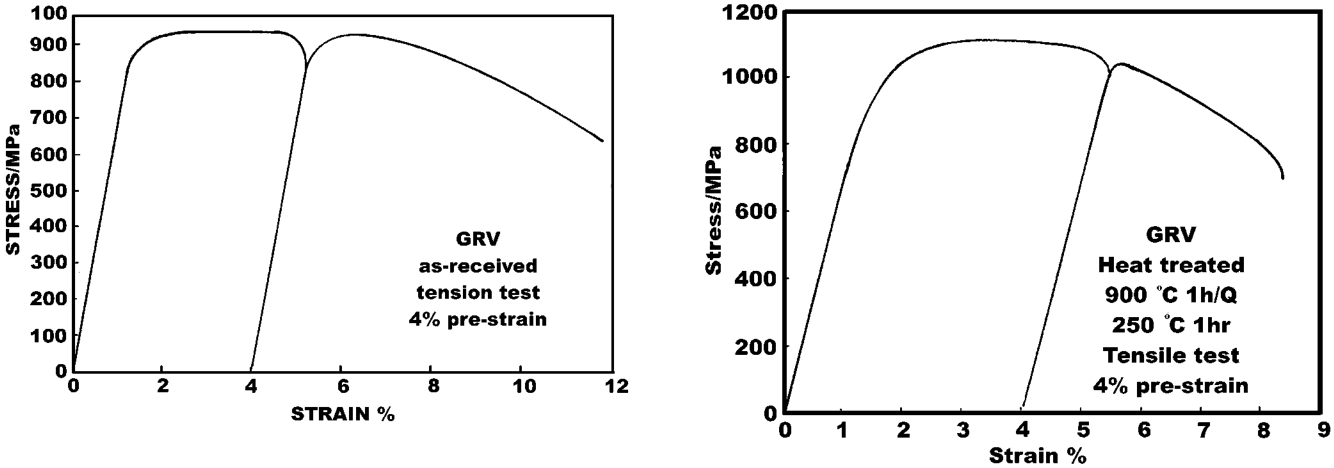
(b)

Fig. 21 **(a)** Effect of prestrain on yield strength in compression (GPQ). **(b)** Effect of prestrain on yield strength in tension (GPQ)

4. Discussion

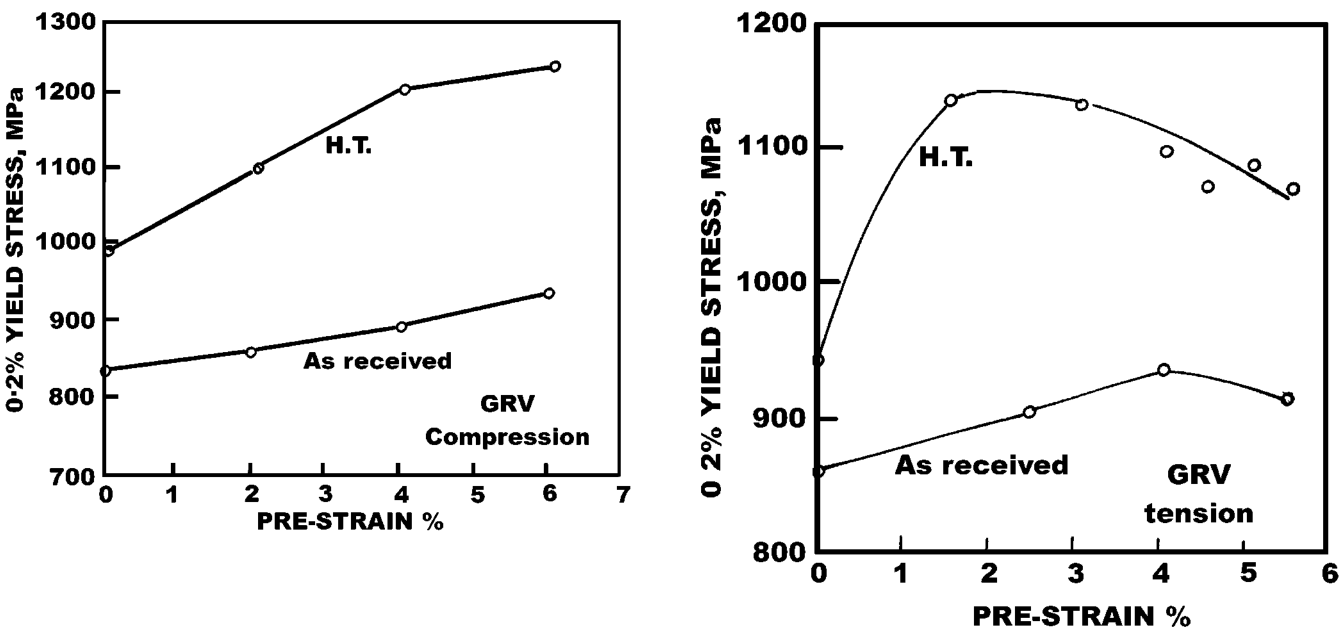
Table 2 gives the mechanical properties of the two Cu-bearing HSLA steels investigated. The structure of GPQ is lath martensite with fine precipitates of copper and globular and needlelike precipitates of carbides of Nb and Ti. The alloy GRV contains low carbon martensite with globular and needlelike precipitates of Nb, Ti, and Fe carbides in addition to elemental copper precipitates. The alloy GPQ contains less copper (1%) and Ni (1.79%) as compared to the alloy GRV (Cu = 1.36% and Ni = 3.46%). Similarly, Cr and Mo of GPQ are also less than those of GRV. Thus, it is found that the yield strength in tension of the GRV is higher than that of alloy GPQ both in the as- received and the heat-treated conditions

The yield strengths in tension for both the materials are generally lower than those in compression. This will result in a ratcheting effect in low-cycle fatigue, and strain accumulation



(a) (b)

Fig. 22 **(a)** Tensile stress-strain behavior of GRV (as received) without and with 4% tensile prestrain. **(b)** Tensile stress-strain behavior of GRV (heat treated) without and with 4% tensile prestrain



(a) (b)

Fig. 23 **(a)** Variation of yield strength with prestrain in compression. **(b)** Variation of yield strength with prestrain in tension

Table 2 Mechanical properties of GPQ and GRV steels

	GPQ		GRV	
Property	**As received**	**Heat treated**	**As received**	**Heat treated**
Yield strength compression (MPa)	840	900	840	980
Yield strength tension (MPa)	620	850	870	940
UTS (MPa)	650	950	930	1100
Fracture strain	20.6%	12%	10%	8%
Hardness (HVN)	230	370	270	370–380
Charpy toughness J	155–160	160–165	190–195	140–145
Fracture toughness MP$\sqrt{m}$	240	290	290	260

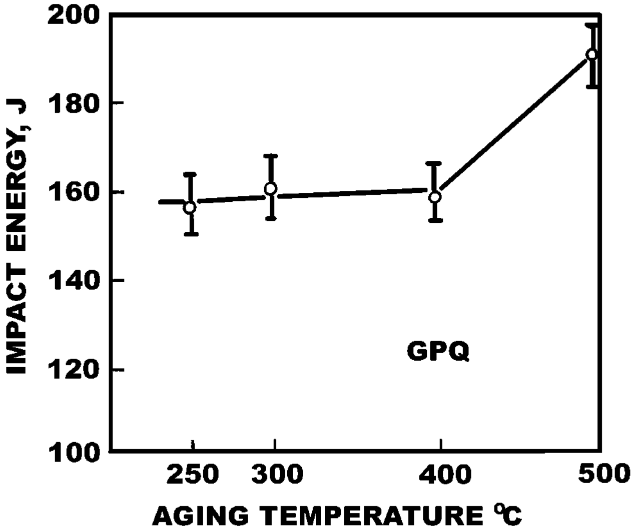


Fig. 24 Variation of charpy impact toughness with aging temperature (GPQ)

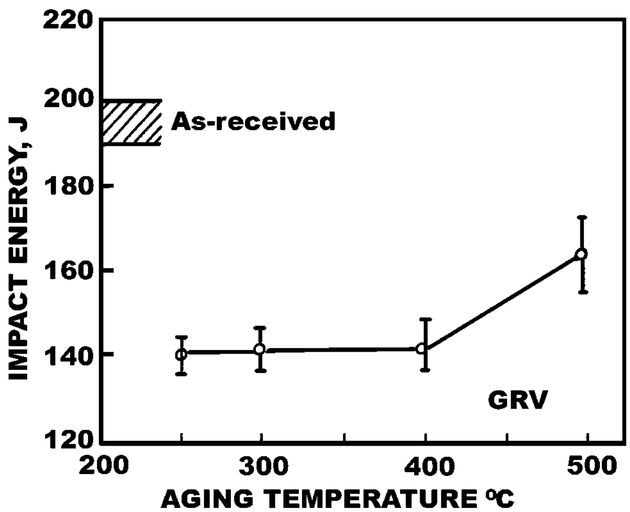


Fig. 25 Variation of charpy impact toughness with aging temperature (GRV)

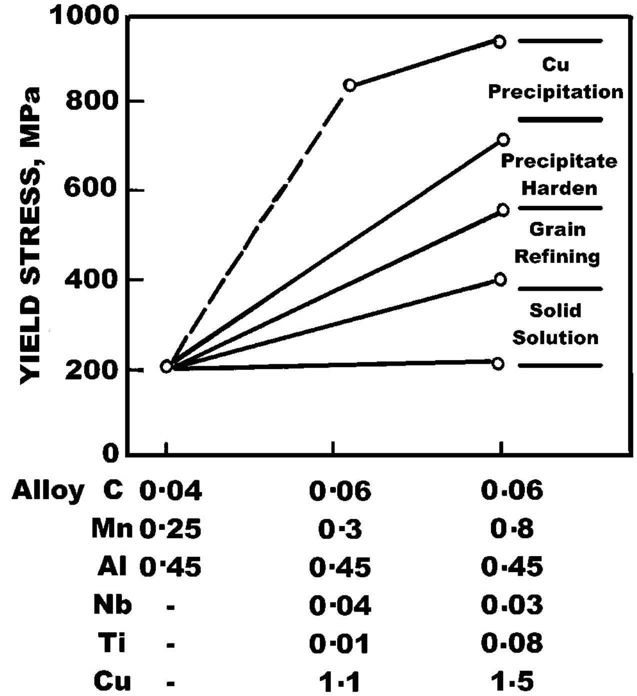


Fig. 26 Mechanisms contributing to strength of alloy steels

during the tensile portion of the cycle will occur, which will alter the dimensions of the structural parts.

The hardness developed at the optimum aging temperature is almost the same, namely, around 370 HVN, and the aging temperature lies in the range of 250 to 350 °C. The increase in strength and hardness at the optimum aging temperature is due to the precipitation of carbides of Nb and Ti and cohesive precipitates of elemental copper of nanometer size. The presence of these precipitates has been identified in the XRD analysis and confirmed by TEM investigations.

Copper will be in solution at the solutionizing temperature of 900 °C. On quenching, it will help to lower the transition temperature (M_s or B_s), and this will lead to an increase in strength during aging. On aging, elemental copper precipitation will occur and the precipitates are of nanometer size of 10 to 50 nm. Their occurrence is controlled by Mo and Cr, and, in the present alloys, the precipitates are coherent. Alloy GRV contains more copper and also Mo and Cr than the alloy GPQ. This is the reason for the better strength and toughness properties of GRV as compared to the alloy GPQ.

The low carbon lath martensite formed imparts high toughness in these alloys. Higher toughness is obtained at higher aging temperatures in the range of 500 to 600 °C, though the alloy GRV has the highest toughness in the as-received condition. Toughness of alloy GRV is better than that of GPQ, though, in general, both of them have high toughness. The increase in toughness is mainly due to the formation of new austenite. Rich new austenite formed at high aging temperature is relatively more stable and does not transform during air cooling of the alloy to room temperature.

A schematic representation of the different mechanisms contributing to the strength of steel due to the addition of alloying elements is shown in Fig. 26. Addition of Nb improves grain refinement and increases the yield strength. Precipitates of titanium and niobium carbides along with other carbides will also contribute to the yield strength. In the case of copper bearing steels, elemental cohesive copper precipitates of nanometer size impart substantial improvement to the yield and ultimate tensile strengths, if proper thermomechanical and aging practices are adopted.

5. Conclusions

From the investigations carried out on two Cu-bearing, HSLA steels, designated as GPQ and GRV, the following conclusions are derived.

- Though the carbon equivalent of the GPQ steel is 0.63%

and that of GRV is 0.8%, these steels can be easily weldable because the carbon content is very low (= 0.05%).

- The solutionized and water-quenched GPQ and GRV exhibit lath martensite with high dislocation density.
- Precipitation of elemental copper of nanometer size is noticeable in both the alloys in the heat-treated conditions. In addition to elemental copper, fine precipitates of carbides and carbonitrides of Nb and Ti are also observed in these alloys.
- As the aging temperature is raised, recovery and recrystallization of the lath structure are observed.
- The alloy content of GRV is more than that of the GPQ and so the precipitation occurring in GRV is more intense than in GPQ.
- Solutionizing and aging in the temperature range of 250 to 350 °C gives the maximum hardness in the range of 350 to 370 VHN for GPQ. For GRV, the maximum hardness is obtained at the aging temperature of 250 °C.
- Prestraining in both compression and tension increases the yield strength of the two steels. However, the increase in compression is more than that in tension.
- Solutionizing and aging increases the charpy impact toughness of both the alloys generally. The maximum is obtained for GPQ when aged in the higher temperature region of 500 °C; however; the maximum toughness is seen in GRV in the as-received condition.
- The values of fracture toughness calculated from the charpy impact toughness values are 290 and 260 MPa$\sqrt{m}$ for GPQ and GRV alloys in the heat-treated condition indicating high resistance to fracture.

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