

Effect of Copper Addition on Grain Refinement of Austenite in Fe-8wt.%Ni-(0-3)wt.%Cu Alloy

(Kesan Penambahan Kuprum terhadap Pengecilan Butiran
Austenit di dalam Aloi Fe-8%bt.Ni-(0-3)%bt.Cu)

JUNAIDI SYARIF* & ZAINUDDIN SAJURI

ABSTRACT

The effect of copper addition on martensitic structure and reversion from martensite to austenite behaviours upon heating were investigated to clarify mechanism of grain refinement of austenite in Fe-8wt.%Ni-Cu alloys. Upon water-quenching, the alloys underwent a martensitic transformation that exhibited a typical lath-martensitic structure. It was found that prior-austenite grain and martensite-packet sizes were refined with increasing copper content. The grain refinement was not due to a decrease of grain growth rate of the austenite. However, it was found that nucleation rate of the austenite on reversion was increased by the copper addition. In Fe-8wt.%Ni alloy heated in (austenite+ferrite) region, reversed austenite grains were formed at high angle boundaries such as prior austenite grain boundary and packet boundary. On the other hand, TEM observation of the Fe-8wt.%Ni-3wt.%Cu alloy revealed that fine copper particles precipitated within the martensitic structure and the reversed austenite grains also formed within lath-structures and lath boundary. It means that the copper addition promoted formation of the reversed austenite within martensitic matrix and resulted in the grain refinement of the prior-austenite in Fe-8wt.%Ni-Cu alloy.

Keyword: Austenite grain; copper addition; grain refinement; refinement martensitic steel; martensitic-austenitic reversion

ABSTRAK

Kesan penambahan kuprum terhadap struktur martensit dan pemedakan butiran kuprum serta kelakuan kebalikan daripada martensit kepada austenit pada pemanasan telah dikaji untuk mengenalpasti mekanisme pengecilan butiran austenit di dalam aloi Fe-8%bt.Ni-Cu. Selepas proses lindap kejut air dilakukan, berlaku penjelmaan martensit pada aloi berkenaan yang dibuktikan melalui kewujudan struktur lazim martensit berbilang. Butiran austenit-terdahulu dan saiz martensit-paket menjadi kecil dengan penambahan kandungan kuprum. Pengecilan butiran bukan disebabkan oleh penurunan kadar pertumbuhan butiran austenit. Sebaliknya, kadar penukleusan austenit daripada proses kebalikan meningkat dengan penambahan kuprum. Untuk aloi Fe8%bt.Ni yang dipanaskan di dalam kawasan fasa-duaan (austenit+ferit), butiran austenit berbalik terhasil pada sempadan sudut tinggi seperti sempadan butiran austenit-terdahulu dan sempadan paket. Daripada sudut yang lain, pencerapan TEM terhadap aloi Fe-8%bt.Ni-3%bt. Cu memperlihatkan butiran halus kuprum termendak di dalam struktur martensit dan butiran austenit berbalik juga terhasil di dalam dan di antara sempadan bilah martensit. Penambahan kuprum memberi kesan kepada pembentukan austenit berbalik di dalam matriks martensit, dan menyebabkan pengecilan butiran austenit-terdahulu pada aloi Fe-8%bt.Ni-Cu.

Kata kunci: Butiran austenit; kebalikan martensit-austenit; keluli martensit; penambahan kuprum; pengecilan butiran

INTRODUCTION

In terms of the promotion of recycling steel scraps, one of tramp elements, i.e. copper, has been tried to be utilised as an effective alloying element for steel in recent years. Copper as an alloying element has the ability to strengthen the steel through precipitation of fine copper particles when copper bearing steels are air-cooled from austenitic phase after solution treatment (Kimura & Takaki 1997) or aged at dual-phase region after quenching (Deschamps et al. 2001; Hornbogen & Glenn 1960). Many studies in copper bearing steels have been concentrated on the precipitation

and strengthening effects of Cu (Deschamps et al. 2001; Nakashima et al. 2002).

On the other hand, authors have investigated the effect of the copper addition on microstructure and hardness in Fe-Cu binary alloys, which were subjected to solution treatment and water-quenching. It is found that the Fe-Cu binary alloy exhibit short-range diffusion transformation, i.e. massive ferritic transformation, and the ferritic grain are refined with increasing copper content. The mechanism of the grain refinement of the ferritic structure in the Fe-Cu binary alloys is due to an increase of driving force of

the massive ferritic transformation and the decrease of grain growth of ferrite through copper addition after the massive ferritic transformation was accomplished (Syarif et al. 2000). If copper addition could be effective to refine microstructure of martensitic steels, which are applied to engineering materials (Krauss 1999), mechanical properties of martensitic steel such as strength and toughness could be improved.

However, phase transformation and morphology of the martensitic structure are more complicated than those of ferritic structure because martensitic transformation of the steel is due to diffusionless and shear process by which a stratified structure is formed. For example, low and medium alloy steels exhibit lath-martensitic transformation, which the structure is characterised by packets that are subdivided to blocks consisting of a large number of laths (Krauss 1990). Moreover, several packets can exist within a single prior-austenite grain. It is understood that the mechanical properties of the martensitic steels have a strong dependency on such kind of structure. For instance, it is well known that hardness and toughness of the martensitic steel could be improved by grain refining of the packet and the prior-austenite (Kim et al. 1998). It is, therefore, important to understand the effect of copper addition on the martensitic structure in utilising the copper bearing martensitic steel.

In this study, the effect of copper addition on the martensitic structure and reversion from martensite to austenite behaviours during heating were investigated to clarify the mechanism of the grain refining of the austenite in the martensitic Fe-8wt.%Ni-Cu alloys.

MATERIALS AND METHODS

Copper bearing steels used in this work have to promote the martensitic transformation on water-quenching from single austenitic region at elevated temperature. Therefore, a third alloying element such as nickel, which is an austenite former element (Honeycombe & Bhadeshia 1995) and can increase hardenability of steels (Moser & Legat 1969) is needed to fulfil the requirement. Figure 1 shows the structure diagram at ambient temperature in relation between nickel and copper concentrations for Fe-Ni-Cu ternary alloy. The steels were subjected to solution treatment at 1273 K for 30 min and then water-quenched. Martensitic single structure could be obtained when nickel

and copper concentrations were more than 7wt.% and up to 3wt.%, respectively. Thus, Fe-8wt.%Ni-(0~3)wt.%Cu alloys (hereafter cited as “8%Ni-(0~3)%Cu steels”) were used as specimens in this work. Chemical compositions of the 8%Ni-Cu steels are listed in Table 1. Ingots of the steels were produced using an induction furnace in a vacuum and then hot-rolled at 1223 K. The steels were solution-treated from 1273 K to 1473 K for 30 to 60 min, followed by water-quenching and then treated at 77 K for 30 min in liquid nitrogen.

Microstructures were observed using an optical microscopy (OM) and a transmission electron microscopy (TEM). The steels were chemically etched with 3% picric acid solution for the OM observation. For TEM observation, film materials were prepared by the twin-jet polishing method using a mixture of 10% perchloric acid and 90% acetic acid solutions. Grain size was determined by comparing the optical micrographs with the ASTM grain size standard (Vander Voort 2007). Martensite-start and -finish temperatures (M_s and M_f temperatures) on cooling were measured using a dilatometer. The steels were machined to cylindrical test pieces of $\phi 3 \times 10$ mm gauge

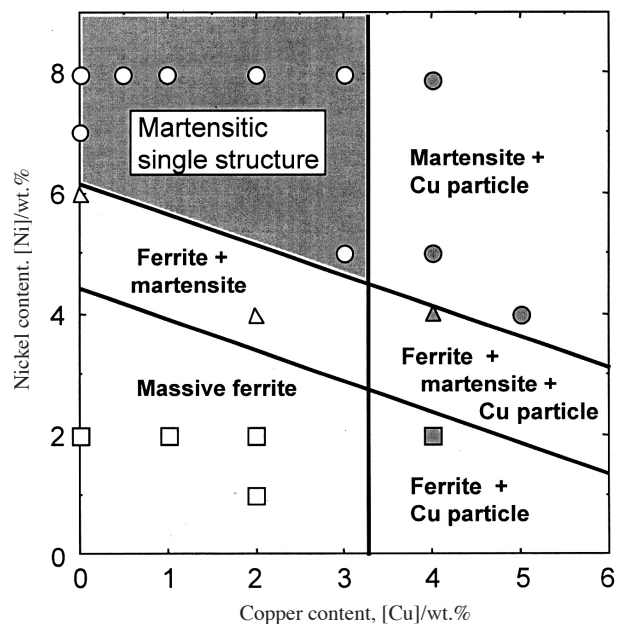


FIGURE 1. Structure diagram of Fe-Ni-Cu alloy at ambient temperature. Specimens were water-quenched after solution treatment of 1273K-30 min

TABLE 1. Chemical compositions of the steels used in this study (wt.%)

	Ni	Cu	C	Si	Mn	Fe
Fe-8%Ni	8.02	<0.01	0.004	<0.01	0.15	bal.
Fe-8%Ni-0.5%Cu	7.94	0.48	0.003	<0.01	0.15	bal.
Fe-8%Ni-1%Cu	8.01	0.92	0.003	<0.01	0.21	bal.
Fe-8%Ni-2%Cu	8.00	1.86	0.003	<0.01	0.13	bal.
Fe-8%Ni-3%Cu	7.92	2.86	0.003	<0.01	0.14	bal.

others; P: 0.010, S: 0.010, N: 0.004

dimension. Then, the steels were heated at 2 K/s, followed by holding at 1273 K for 2 min and then cooled at 20 K/s. Lattice parameters of matrix were evaluated by means of X-ray diffractometry. Concentrations of elements at grain boundary of austenite were measured by an Auger electron spectrometry (AES). The specimen was subjected to impact test at temperature of liquid nitrogen to induce grain-boundary fracture. Precipitation of copper particles and reversion behaviours on heating were investigated using a differential scanning calorimeter (DSC) in an argon atmosphere at a heating rate of 20 K/s.

RESULTS AND DISCUSSION

MICROSTRUCTURE OF AS-QUENCHED FE-8%NI-CU ALLOYS

Figure 2 shows the change in M_s and M_f temperatures of the 8%Ni-Cu steels, plotted as a function of copper content. The M_s and M_f temperatures decreased with increasing copper content and decrement of the temperatures was around 10 K/wt.%. The M_f temperatures were sufficiently higher than ambient temperature in all of the steels therefore, it was thought that no austenitic phase was retain within the martensitic matrix in the 8%Ni-Cu steels.

It is well known that the morphology of the martensitic structure is strongly dependent of alloying elements and prior-austenite grain size (Morito et al. 2003; Takaki et al. 2004), and thus, to evaluate the effect of the copper addition only on the morphology of the martensitic structure, the prior-austenite grain size should be set at the same size. Figure 3 shows the optical and transmission electron micrographs of the 8%Ni-Cu steels, where the prior-austenite grains were controlled to be about 200 μm . The prior-austenite grain sizes were controlled by

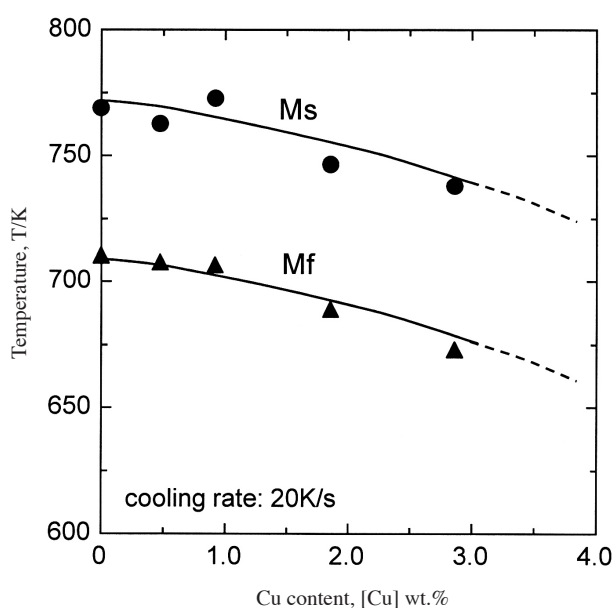


FIGURE 2. Change in M_s and M_f temperatures of 8%Ni-Cu steels as a function of copper content

changing temperature and holding time of the solution treatment. The as-quenched 8%Ni-Cu steels exhibited a typical lath-martensitic single structure composed of martensite-packet, -block and -lath structures. TEM micrograph and measurement of lattice parameter of martensitic matrix using X-ray diffractometry suggested that alloying elements such as carbon, copper and nickel were in super-saturated solid solution. It was found that packet-sizes and block-width were almost the same and no significant difference was observed in the morphology of the lath-martensitic structure in the specimens. It means that the effect of copper addition was not significant on the morphology of the martensitic structure in the 8%Ni-Cu steel. On the other hand, it is believed that copper addition could influence the size of the prior-austenite grain on solution treatment. Figure 4 shows the optical micrographs of the as-quenched specimens of 8%Ni steel (a), 8%Ni-1%Cu steel (b) and 8%Ni-3%Cu steel (c). The steels were subjected to solution treatment at 1273 K for 30 min then water-quenched and treated at 77 K. It was found that the prior austenite grains and the martensite-packets were refined owing to the copper addition. The relation between the prior-austenite grain size and copper content in the 8%Ni-Cu steels is shown in Figure 5. The specimens were etched by a solution consisting of saturated aqueous picric acid, dodecylbenzenesulfonate and HCl to reveal prior-austenite grain boundary for measuring prior-austenite grain size. The prior-austenite grains gradually refined with increasing copper content up to 3wt.% at decrement of 60 μm /wt.%. For instance, the prior-austenite grain size of the 8%Ni steel could be refined from 270 μm to 100 μm by addition of 3wt.%Cu.

MECHANISM OF THE GRAIN REFINEMENT OF AUSTENITE BY COPPER ADDITION

Since copper atoms were in super-saturated solid solution in austenitic matrix during the solution treatment, the grain refinement of the austenite in the 8%Ni-Cu steel could not be explained by a grain-boundary pinning effect of copper particles. Therefore, the grain refinement of austenite might be due to the increase in nucleation rate of the austenite on heating or the decrease in grain growth rate of the austenite at solution-treatment temperature.

EFFECT OF SOLUTE COPPER ON GRAIN GROWTH OF AUSTENITE

It was reported that the prior-austenite grains are refined with increasing copper content in martensitic Fe-9%Cr-Cu alloys and that copper atoms segregated up to 57at.% into the austenite grain boundary in the martensitic Fe-9%Cr-4%Cu alloy (Futamura et al. 1999). Hence, the segregation of the copper retards the grain growth of the austenite at temperature of the solution treatment and leads to the grain refinement of the austenite in the martensitic Fe-9%Cr-Cu alloys. To clarify the segregation of the copper atoms in the austenite grain boundary and its effect on the grain growth of austenite, copper and other elements

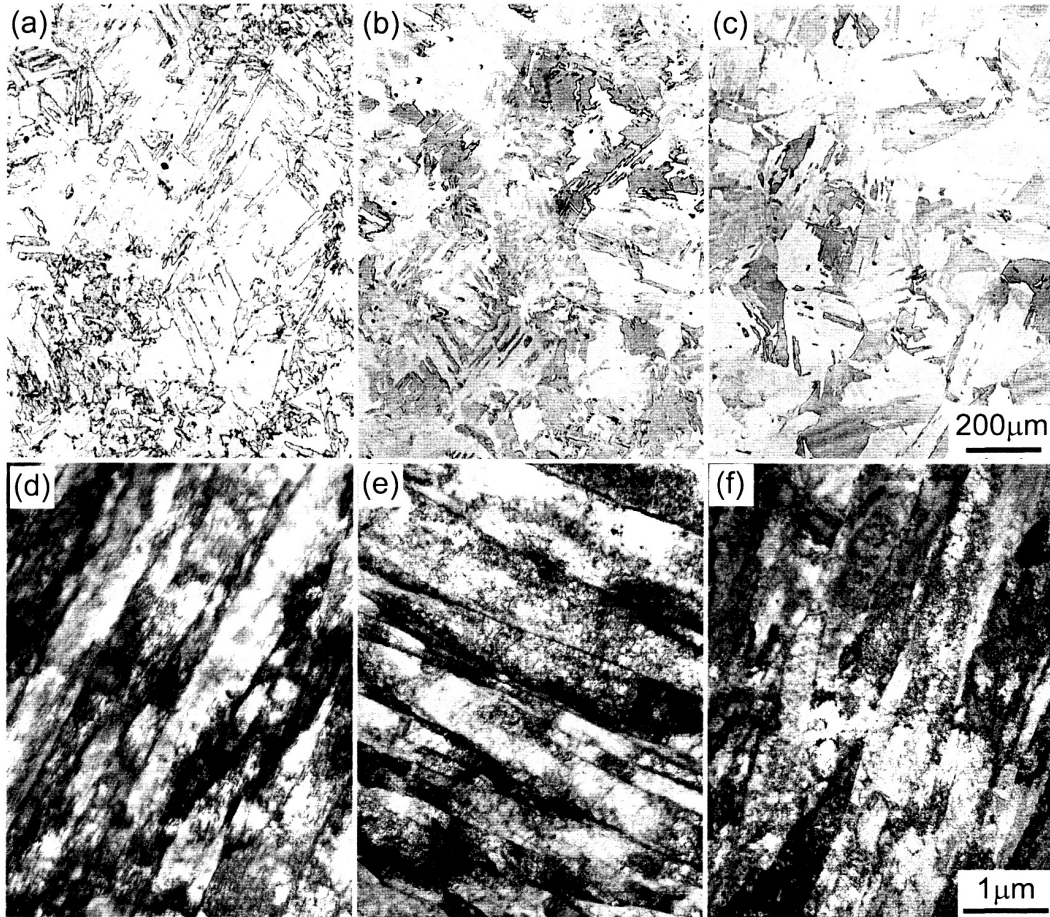


FIGURE 3. Optical and TEM micrographs of as-quenched specimens of 8%Ni steel (a) (d), 8%Ni-1%Cu steel (b) (e) and 8%Ni-3%Cu steel (c) (f). The prior-austenite grain sizes were controlled to be about 200 μm



FIGURE 4. Optical micrographs of 8%Ni steel (a), 8%Ni-1%Cu steel (b) and 8%Ni-3%Cu steel (c). The steels were subjected to solution treatment at 1273 K for 30 min, then water-quenched and subzero treated at 77 K

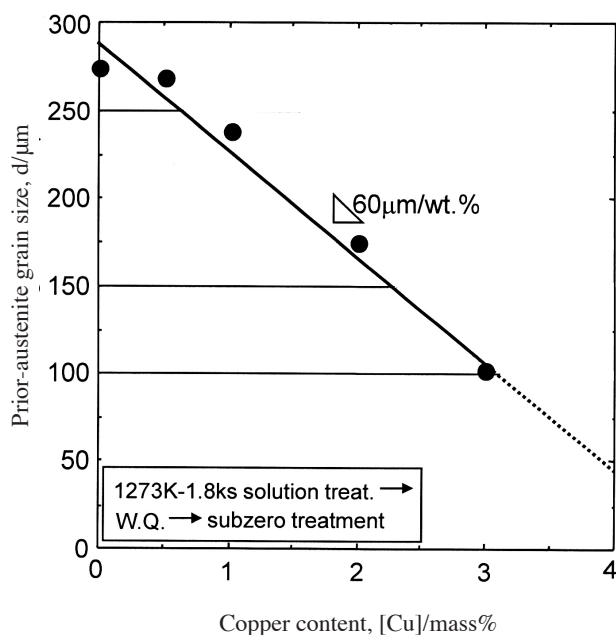


FIGURE 5. Relation between the prior-austenite grain size and copper content in 8%Ni-Cu steels. The specimens were subjected to solution treatment at 1273 K for 30 min and then water-quenching and subzero treatment

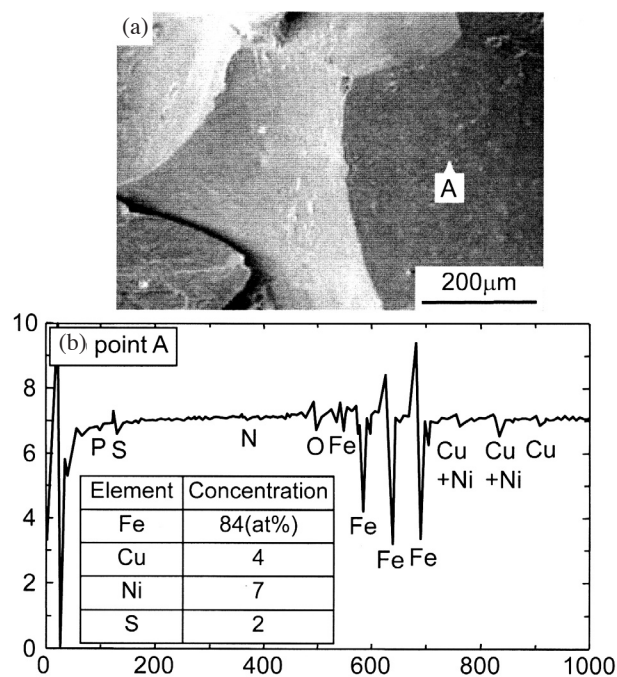


FIGURE 6. (a) A scanning electron micrograph of surface of grain-boundary fracture and (b) an Auger electron spectrum obtained from point A

concentrations were measured using the AES in the 8%Ni-Cu steel. Figure 6 shows the scanning electron micrograph revealing surface of grain-boundary fracture of the 8%Ni-3%Cu steel (a) and an Auger electron spectrum obtained from point A (b). The elements concentrations on the austenite grain boundary were obtained from the

spectrum. It was found that the copper segregated into the austenitic grain boundary up to 4at% (4.5wt.%) in the 8%Ni-3%Cu steel. However, the concentration of the segregated copper atoms in the 8%Ni-3%Cu steel was obviously smaller than that in the martensitic Fe-9%Cr-4%Cu alloy, which the copper atoms segregates up to 57at.% into the austenite grain boundary (Futamura et al. 1999). Although it is still unclear why the concentration of the segregated copper atoms in the 8%Ni-Cu steel was small, it was thought to be due to next-stated reason: an increase of solubility of copper in austenite phase owing to strong interaction between copper and nickel atoms (Salter 1966).

Figure 7 shows the change in the austenite grain size of the 8%Ni-Cu steels as a function of holding time at 1273K to investigate effect of the segregated copper atoms on the grain growth of the austenite. The changes in the austenite grain sizes exhibited a linear relation with square root of holding time, and thus, it was consistent with the normal grain growth behaviour (Burke & Turnbull 1952). Because grain growth rates, which correspond to graph's slope, were almost the same in all steels, the grain growth rates of the steels were almost independent of the copper addition. Conversely, there was a significant difference in the austenite grain sizes just after reached to the solution treatment temperature: the grain sizes were extrapolated to the time of 0s. The austenite grain sizes became smaller with increasing copper content. This indicated that the grain refining of the austenite was not influenced by the grain-boundary dragging effect of the copper atoms, but strongly affected by the increase in the nucleation rate of the reversed austenite on heating through the copper addition.

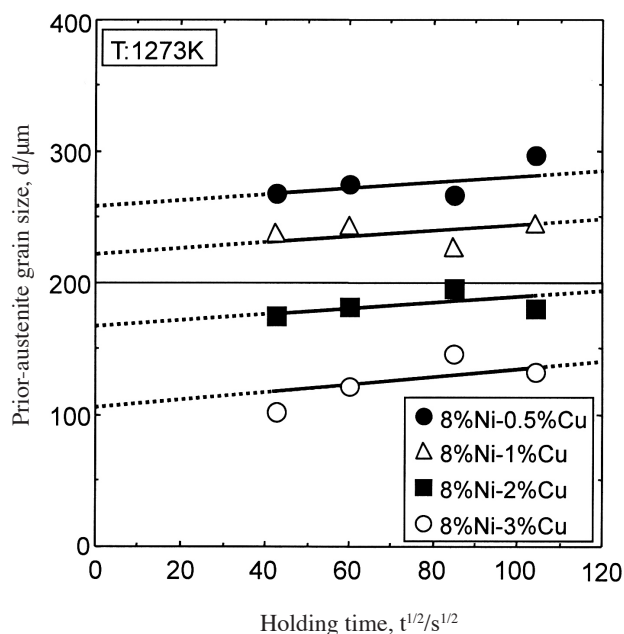


FIGURE 7. Relation between holding time of solution treatment and the prior-austenite grain size in 8%Ni-Cu steels. The specimens were subjected to solution treatment at 1273 K

CHANGE IN NUCLEATION RATE OF AUSTENITE DUE TO
COPPER ADDITION

To clarify the effect of the copper addition upon the nucleation rate of the reversed austenite upon heating, at first, the precipitation behaviour of the copper particles on heating was examined by DSC thermal analysis in the 8%Ni-3%Cu steel. Figure 8 shows a DSC curve of the 8%Ni-3%Cu steel, which was heated at 20 K/s. Exothermic and endothermic peaks were observed in the vicinity of 850 K and 1000 K, respectively. The exothermic peak was identified as the precipitation of the copper particles. On the other hand, the endothermic peak was the reversion from martensite to austenite. It means that the copper particles precipitated within the martensitic matrix before the reversion upon heating. Figure 9 shows the optical micrograph of partially reversed 8%Ni steel and schematic illustration. The steels were reheated to 960 K, which is a (ferrite+austenite) dual-phase region, and then air-cooled to result in partial reversion of austenite in martensitic matrix. Reversed austenite grains, which existed as fresh martensitic structure at ambient temperature after water-quenching, and untransformed martensitic structures were shown in white and gray areas, respectively. It was found that the reversed austenite grain was formed at high angle boundary such the prior-austenite and the packet boundaries. The 8%Ni-3%Cu steel, which was heat-treated at the same condition, also revealed almost similar feature. Figure 10 represents the result of further observation using TEM and schematic illustrations for the 8%Ni (a) (c) and 8%Ni-3%Cu steels (b) (d). In the 8%Ni steel, it was observed that dislocation density was decreased and subgrain structure was formed. Thus, it means that recovery of lath structure occurred during heating. However, no reversed austenite grain was

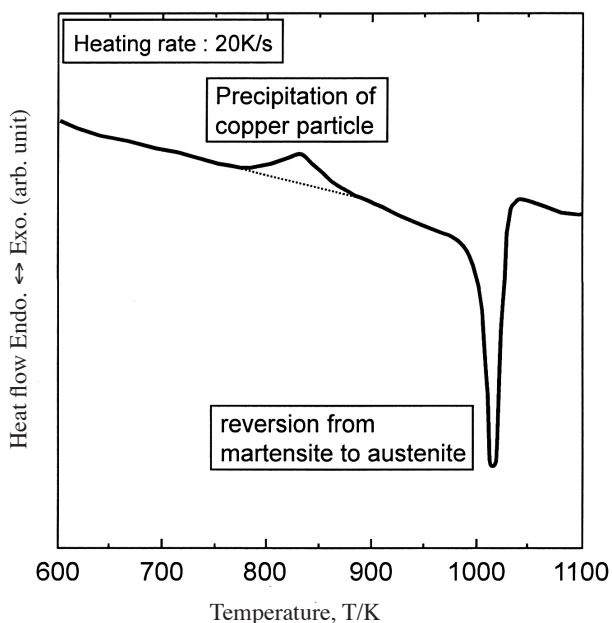


FIGURE 8. DSC thermograph of the 8%Ni-3%Cu steel

observed within the martensite-lath or at lath-boundary, although it was formed on the prior-austenite grain and packet boundaries. Conversely, in the 8%Ni-3%Cu steel, a large number of fine copper particles with the size of 20 nm in diameter precipitated within the martensite-lath and furthermore the reversed austenite grains with the size less than 1 μm were formed on the lath boundaries.

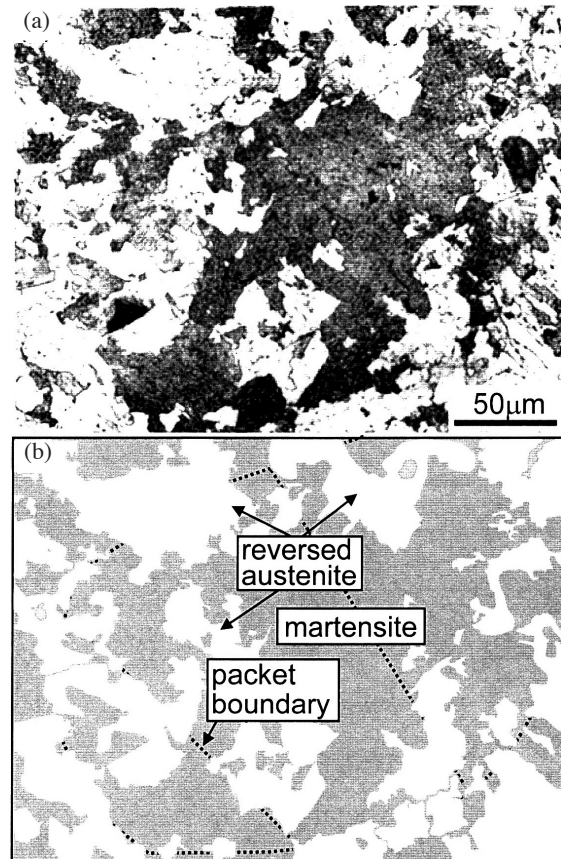


FIGURE 9. Optical micrograph (a) and schematic illustration (b) of partially reversed 8%Ni steel. The steel was reheated to 960 K, which is a (ferrite+austenite) dual-phase region, and then air cooled

It was thought that the reversed austenite grain could nucleate within martensite-lath and at the lath boundary because the copper particles, which precipitated before reversion upon heating, provided an effective nucleation site for the reversed austenite grain. Since copper is an austenite former element, the copper particles should partially dissolve at elevated temperature and the copper concentration should increase at interface of the copper particles and martensitic matrix. Hence, such kind of region was thought to be an effective nucleation site for the reversed austenite grain. That is to say that the nucleation rate of the reversed austenite, which formed within the martensitic matrix, was increased owing to the copper addition and this led to the grain refinement of the prior-austenite in the as-quenched 8% Ni-Cu steel. Although the

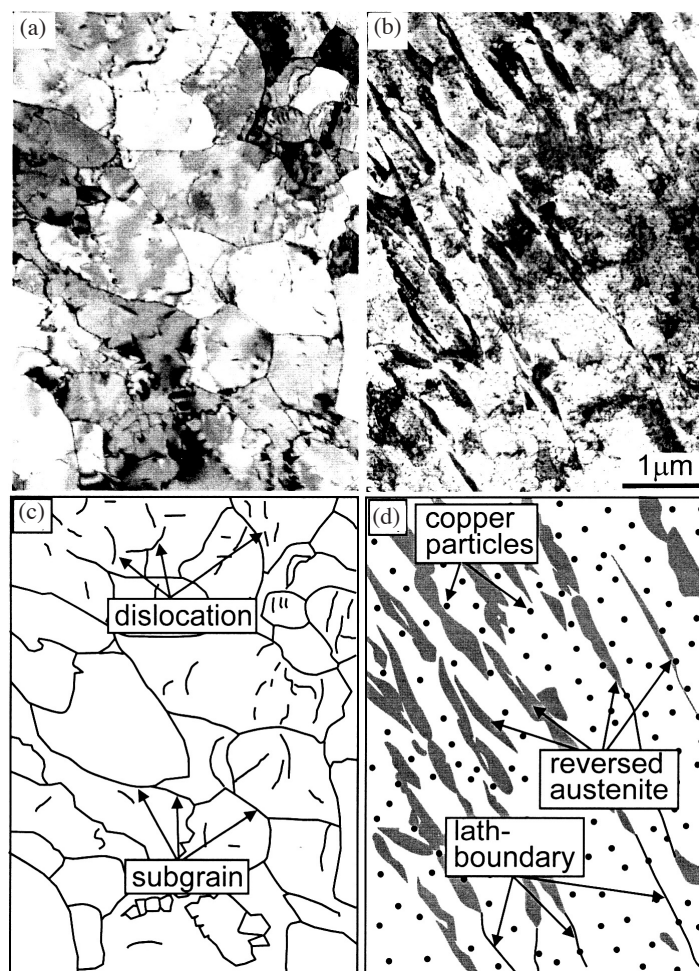


FIGURE 10. TEM micrographs and schematic illustration of partially reversed the 8%Ni (a) & (c) and the 8%Ni-3%Cu steels (b) & (d)

reversed austenite grains can be coalesced one another and coarsen during reversion on heating (Tsuchiyama et al. 1998), it was thought that the number of reversed austenite grain should be increased when the reversion accomplished and thus the grain refinement of the austenite would occur after water-quenching.

CONCLUSION

The investigation on effect of copper addition on the martensitic structure and the grain refining of the austenite in the Fe-8wt.%Ni alloy led to the conclusion as follows. Microstructures of as-quenched 8wt.%Ni-Cu steels had typical lath-martensitic structure. The morphology of the martensite-lath was independent of the addition of copper. However, the prior-austenite grains were refinement through the copper addition. The grain refining of prior-austenite was due to the increase in the nucleation rate of the austenite grain on reversion. However, the grain-boundary dragging effect of the copper atoms had small influence on the grain refining of the prior-austenite. Copper particles finely precipitated within martensite-

lath in martensitic structure upon heating, and provided the nucleation sites for reversed austenite grain. Thus, the nucleation rate of the reversed austenite was promoted through the copper addition.

REFERENCES

- Burke, J.E. & Turnbull, D. 1952. Recrystallization and Grain Growth. *Prog. in Met. Phys.* 3: 220-244.
- Deschamps, A., Militzer M. & Poole, W.J. 2001. Precipitation kinetics and strengthening of a Fe-0.8wt%Cu alloy, *ISIJ International* 41: 196-205.
- Futamura, Y., Tsuchiyama, T. & Takaki, S. 1999. Effect of Cu addition on phase transformation and microstructure in 9 mass% Cr martensitic steels. *Tetsu- to-Hagané* 85: 697-702.
- Honeycombe, R.W.K & Bhadeshia, H.K.D.H. 1995. *Steels: Microstructure and Properties*. London: Edward Arnold.
- Hornbogen, E. & Glenn, R.C. 1960. A metallographic study of precipitation of copper from alpha iron. *Trans. AIME*. 218: 1064-1070.
- Kim, H.J., Kim, Y.H. & Morris Jr, J.W. 1998. Thermal mechanisms of grain and packet refinement in a lath martensitic steel. *ISIJ International* 38: 1277-1285.

- Kimura, Y. & Takaki, S. 1997. Phase transformation mechanism of Fe-Cu alloys, *ISIJ International* 37: 290-295.
- Krauss, G. 1990. *Steel Heat Treatment and Processing Principles*, Materials Park (OH): ASM International.
- Krauss, G., 1999. Martensite in steel: Strength and structure, *Materials Sci. & Eng. A273-275*: 41-57.
- Morito, S., Tanaka, H., Konishi, R., Furuhashi, T. & Maki T. 2003. The morphology and crystallography of lath martensite in Fe-C alloys, *Acta Materialia* 51: 1789-1799.
- Moser, A. & Legat, A. 1969. Calculation of hardenability from composition. *Haertere-Technische Mitteilungen* 24: 100-105.
- Nakashima, K., Futamura, Y., Tsuchiyama, T. & Takaki, S. 2002. Interaction between dislocation and copper particles in Fe-Cu alloys. *ISIJ International* 42: 1541-1545.
- Salter, W.J.M. 1966. Effects of alloying elements on solubility and surface energy of copper in mild steel. *J.Iron and Steel Inst.* 204: 478-488.
- Syarif, J., Hoshino, T., Tsuchiyama, T. & Takaki, S. 2000. Effect of solute copper on hardness and ductile-to-brittle transition in α -iron. *Tetsu- to-Hagané* 86: 558-562.
- Takaki, S., Fukunaga, K., Syarif, J. & Tsuchiyama, T. 2004. Effect of grain refinement on thermal stability of metastable austenitic steel. *Materials Trans.* 45: 2245-2251.
- Tsuchiyama, T. & Takaki, S. 1998. Formation of reversed austenite from $M_{23}C_6$ type High Chromium Martensitic Steel, *Proceeding of the Third Pacific Rim International Conference on Advanced Materials and Processing (PRICM3)*. 1: 1187-1192.
- Vander Voort, G.F. 2007. *Metallography, Principles and Practice*. Ohio: ASM International.

Department of Mechanical and Materials Engineering
Faculty of Engineering and Built Environment
Universiti Kebangsaan Malaysia
43600 UKM Bangi, Selangor
Malaysia

*Corresponding author; email: syarif@eng.ukm.my

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