

The Vacancy-hardening Properties in Water-quenched Fe-Al Alloys

Z. C. ZHOU^a, J. DU^b, Y. K. ZHANG^c, Y. P. ZHANG^d, S. Y. GU^e

School of Mechanical and Electronic Engineering, Suzhou Vocational University, Suzhou, 215104, China

^azcc@jssvc.edu.cn, ^bduj@jssvc.edu.cn, ^czyk@jssvc.edu.cn, ^dzyp@jssvc.edu.cn, ^egsy@jssvc.edu.cn

Keywords: Vacancy-hardening, Heat Treatments, Water-quenched Fe-Al Alloys.

Abstract. Fe-Al alloys with different Al contents were prepared with commercially pure Fe and Al in a vacuum induction furnace. The hardness of the Fe-Al alloys with different Al content and heat treatments was measured using a Vickers-hardness tester of HVS-5, applying a load of 9.8 N and keeping for 8 s. In order to detect the lattice strain of the specimens, X-ray diffraction (XRD) experiments with CuK_α radiation ($\lambda=1.5406 \text{ \AA}$) were completed at room temperature for $\text{Fe}_{62}\text{Al}_{38}$ specimen with different heat treatments. It was shown that the hardness of the furnace-cooled Fe-Al alloys increases with increasing Al content when Al content is less than 23 (at.%) Al and then decreases when more than 23 (at.%) Al. The furnace-cooled $\text{Fe}_{77}\text{Al}_{23}$ alloy has the largest hardness value among all furnace-cooled alloys. The effect of quenching on the hardness of the $\text{Fe}_{77}\text{Al}_{23}$ and $\text{Fe}_{71}\text{Al}_{29}$ alloys can be obviously observed. The hardness of the $\text{Fe}_{62}\text{Al}_{38}$ alloy increases obviously with increasing quenching temperature. The hardening effect resulted from thermal vacancies can be reduced by the ageing at low temperature.

Introduction

Fe-Al alloys contain large numbers of atomic defects such as vacancies and antisite atoms. The defects have great effect on the mechanical and physical properties. Schaefer et al [1-2] studied vacancy features of Fe-Al alloys by positron lifetime spectroscopy and mechanical relaxation spectroscopy. Chang et al [3] calculated the vacancy concentration as a function of temperature and Al content. Würschum et al [4] studied the formation and migration of vacancies at high temperatures in B2-type Fe-Al alloys. Indeed, atomic defects in metals or intermetallic compounds under thermal equilibrium play an important role in many solid state processes at high temperature such as order-disorder transition [5], self-diffusion [6] and mechanical creep etc [7]. It is therefore necessary to make clear the effect of the defects for understanding the evolvement of the microstructure and effect of the defects on mechanical properties. From the reported results, quite many researches are focused on the atomic defects, e.g. vacancies, of the Fe-Al alloys. Recently, Čížek et al [8] investigated the vacancies in Fe_3Al by positron annihilation and Zhao et al [9] analyzed thermal vacancy behavior in B2-type FeAl through thermal expansion, lattice parameter, and elastic modulus measurements. In addition, there are many researches involved in the relaxation caused by atomic defects in Fe-Al alloys [10-11].

It has been known that concentration of the constitutional defects is sensitive to the alloy composition but is independent of temperature [12] and the concentration of thermal defects, e.g. thermal vacancies have strong dependence on temperature [4]. Nevertheless, it is not completely clear what changes in thermal defects may take place with Al content and heat treatments, and what correlations of the mechanical properties and thermal vacancies (and/or other atomic defects) may exist. The present work presents the variation of the Vickers hardness of Fe-Al alloys with Al content and heat treatments, finding the correlations among the Vickers hardness, vacancy, Al content in water-quenched Fe-Al alloys.

Experimental Procedure

Fe-Al alloys with Al content (at.%) of 11, 17, 23, 29 and 38 (all compositions are described in terms of atomic percent in this article, unless described specially) were prepared with commercially

pure Fe and Al in a vacuum induction furnace. The specimens used in the hardness measurements were cut from the ingots into a dimension $10 \times 10 \times 2 \text{ mm}^3$ using an electric sparkle machine. The specimens with different Al content were heated to 700 °C, 800 °C, 900 °C and kept for one hour in an argon atmosphere, followed by water-cooling. In addition, the specimens are also heated for 4 hour at 900°C and furnace cooled and the specimen that is water-quenched from 800 °C is aged at 350 °C for different time. Specimen surfaces were ground using silicon carbide papers to a 500 grit finish before the hardness of all specimens were measured.

The Vickers-hardness of the specimens with different Al content and heat treatments was measured using a Vickers-hardness tester of HVS-5, applying a load of 9.8 N and keeping for 8 s. Standard deviations of Vickers hardness were typically $\pm 3\text{-}5 \text{ Hv}$. In order to detect the lattice strain change for the $\text{Fe}_{62}\text{Al}_{38}$ specimens with different heat treatments, X-ray diffraction (XRD) experiments with CuK_α radiation ($\lambda=1.5406 \text{ \AA}$) were completed at room temperature for $\text{Fe}_{62}\text{Al}_{38}$ specimen with different heat treatments.

Results and Discussion

The Variation of Vickers Hardness with Al Content

Fig. 1 shows the variation of Vickers hardness with Al content for furnace-cooled Fe-Al specimens. It can be seen that the hardness increases initially with increasing Al content and decreases when Al content is over 23(at.%) . The hardness peak value appears in the furnace-cooled 23 (at.%)Al alloy. The initial hardness increase is attributed to the effect of solid solution strengthening of Al on the Fe-Al alloys. It is well known that the effect of solid solution strengthening increases with increasing the concentration of solid atoms and therefore the hardness of furnace-cooled Fe-Al alloys increases with increasing Al content. The furnace-cooled $\text{Fe}_{77}\text{Al}_{23}$ alloy has largest hardness value among all alloys with different Al content, which is similar to the results reported by Hasemann et al [13], who found the maximum of yield stress occurs in the slow-cooled specimen with 25 (at.%) Al. When Al content is over 23 (at.%) , the hardness is reduced for the furnace-cooled Fe-Al alloys. According to Ref. [14], the dilute Fe-Al alloys with the Al content from 0 to 22% are intrinsically disordered A2 structure according to Fe-Al phase diagram. When Al content is located between 23 and 36 (at. %), the ordered Fe_3Al with D_{03} structure can be formed and ordered D_{03} structure can enhance the hardness of Fe-Al alloys. The deviation from stoichiometry can in principle be compensated for either by vacancy or by antisite atom [15]. For $\text{D}_{03} \text{Fe}_3\text{Al}$, on one hand, structural defects on the rich-Fe side are Fe antisite atoms and on the rich-Al side are Al antisite atoms for the furnace-cooled alloys due to little thermal defects. Therefore, the furnace-cooled $\text{Fe}_{77}\text{Al}_{23}$ alloy has higher hardness value than $\text{Fe}_{71}\text{Al}_{29}$ alloy since the former contains Fe antisite atoms and the latter has Al antisite atoms for the two alloys with the same D_{03} structure. More Al antisite atoms decrease the hardness of $\text{Fe}_{71}\text{Al}_{29}$ alloy since Al has smaller hardness than Fe. In addition, From Table 1, it can be seen that heating temperature has smaller effect on the hardening of the water-quenched alloys with lower Al content since the water-quenched alloys with lower Al content have less vacancy concentration.

Tab. 1 The Vickers Hardness Values of Specimens with Different Al Concentration and Heat Treatment

Al (at. %)	Vickers hardness (MPa)				
	700 °C-WQ*	800 °C-WQ	900 °C-WQ	900 °C-FC	350 °C-20h-aged
11	193	199	196	200	
17	267	280	281	299	
23	303	309	317	351	340
29	283	299	308	284	
38	313	381	411	276	

* WQ denotes water quenching and FC denotes furnace cooling

Fig. 2 present the variation of Vickers hardness with Al contents for the water-quenched specimens. It can be seen that the hardness of the specimens increases with increasing Al contents when Al content is less than about 23 (at.%).

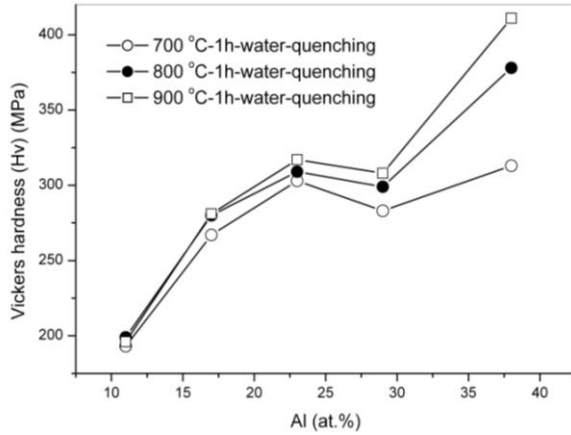


Fig. 1 The Variation of Vickers Hardness with Al Content for Furnace-cooled Fe-Al Specimens

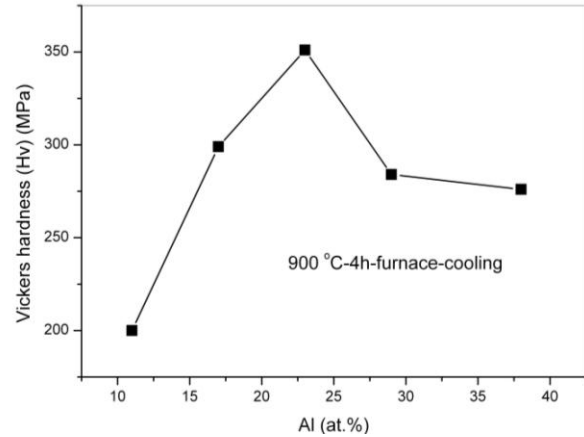


Fig. 2 The Variation of Vickers Hardness with Al Content for Water-quenched Fe-Al Specimens from Different Temperature

From Figs. 1, 2 and Table 1, it can also be seen that the Vickers hardness of the furnace-cooled $\text{Fe}_{77}\text{Al}_{23}$ alloy has the higher value than the water-quenched specimens with the same chemical compositions. This is attributed to the increase of order degree in the furnace-cooled. D0_3 structure formed during the furnace-cooling possesses higher hardness than A2 structure. According to Ref. [16], D0_3 ordering treatment is generally carried out in the temperature range from 200 °C to 500 °C. Further investigation shows the aging at low temperature for long time has the similar effect to the furnace-cooling from high temperature. The Vickers hardness value can be increased to 340 MPa by the ageing at 350 °C for 20 hours for the $\text{Fe}_{77}\text{Al}_{23}$ alloy.

In addition, it can be noticed that the Fe-Al alloys with the compositions in the vicinity of Fe-25 at.% Al can hardly be strengthened by the water-quenching. The Vickers hardness is increased a little for the water-quenched $\text{Fe}_{77}\text{Al}_{23}$ and $\text{Fe}_{71}\text{Al}_{29}$ alloys compared with the furnace-cooled alloys. However, the hardness of the $\text{Fe}_{62}\text{Al}_{38}$ alloy with B2 structure increases drastically with increasing quenching temperature, as shown in Fig. 1. The hardness increase is resulted from the thermal vacancy-hardening. The vacancy concentration in $\text{Fe}_{77}\text{Al}_{23}$ and $\text{Fe}_{71}\text{Al}_{29}$ with potential D0_3 structure is much smaller than that of the $\text{Fe}_{62}\text{Al}_{38}$ alloy with B2 structure according to Refs. [15-18]. It has been known that the vacancy concentration in materials increases with increasing temperature and the hardness will be increased if the vacancies is retained by the quenching. Therefore, the Vickers hardness increases with increasing quenching temperature.

It is easily understood that the lattice constant is reduced when the vacancies are introduced into the alloys. The reduction in lattice constants will shift the diffraction peak to higher angle according to Bragg law in X-ray diffraction experiments [19]. According to Ref. [20], the relation of the lattice strain and the diffraction angle can be described as the following equation:

$$\frac{\beta_{hkl}^2}{\tan^2 \theta_{hkl}} = \frac{\lambda \beta_{hkl}}{D_{hkl} \tan \theta_{hkl}} + 16 \langle \varepsilon_{hkl}^2 \rangle^{\frac{1}{2}} \quad (1)$$

Where, λ is wavelength of Cu $\text{K}\alpha$ radiation. D_{hkl} and $\langle \varepsilon_{hkl}^2 \rangle^{\frac{1}{2}}$ is grain size and lattice strain on $\langle hkl \rangle$ direction, respectively. β_{hkl} is a width coefficient and θ_{hkl} is diffraction angle on $\langle hkl \rangle$ direction. From equation (1), it can be also seen that the $\langle \varepsilon_{hkl}^2 \rangle^{\frac{1}{2}}$ is related to θ_{hkl} . The present

experiments are in agreement with Refs. [20-21]. From Fig. 2, the (110) diffraction peak of the water-quenched $Fe_{62}Al_{38}$ alloy is shifted to higher angle compared with the furnace-cooled $Fe_{62}Al_{38}$ alloy since the water-quenched $Fe_{62}Al_{38}$ alloy contains large numbers of vacancies, which reduces the lattice constants and increases the diffraction angle. From Fig. 2, it can also be seen that curve 2 in Fig. 2 is a little not symmetric obviously. This asymmetry can be resulted from the heterogeneity of lattice strain caused by vacancies.

The Variation of Vickers Hardness with Aging Time

Generally, the thermal vacancies can be annihilated when the quenched specimens are aged at low temperature. Fig. 3 and Table 2 show the hardness variation of the 800 °C-water-quenched $Fe_{62}Al_{38}$ alloy with ageing time at 350 °C [16-17]. It can be seen that the hardness decreased with increasing the ageing time. It has been reported that the vacancy annihilation can produce dislocation in B2 FeAl alloys, which has a little contribution to hardness [16], indicating that the vacancy-hardening is reduced and the vacancy concentration is gradually decreased. Further investigation shows the hardness of the water-quenched $Fe_{62}Al_{38}$ alloy from 900 °C is decreased from 411 Hv to 307 Hv when aged at 400 °C for 2.5 hours, indicating that higher ageing temperature has stronger reducing effect on hardness under the same ageing time.

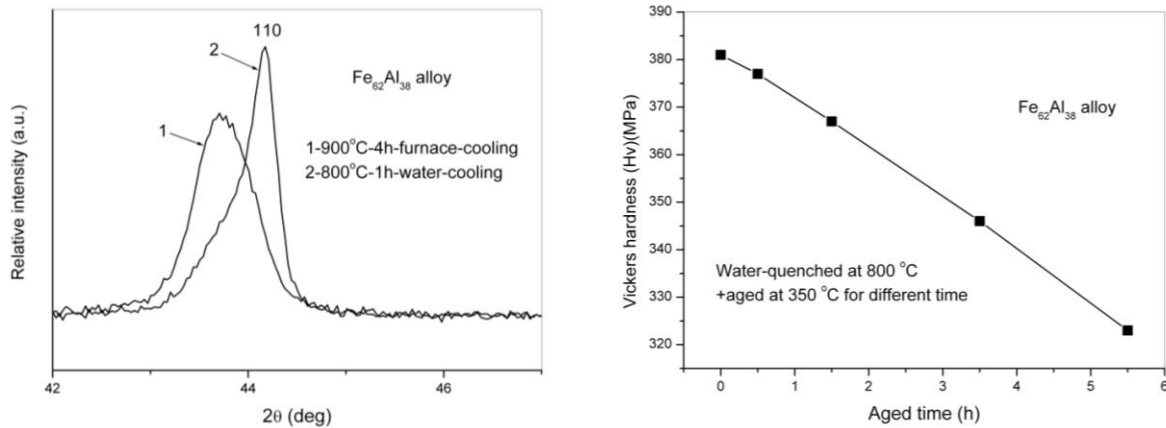


Fig. 3 The X-ray Profiles of the Water-quenched and Furnace-cooled $Fe_{62}Al_{38}$ Specimens Fig. 4 The Variation of Hardness with Ageing Time for the Water-quenched $Fe_{62}Al_{38}$ Alloy from 800 °C

Tab.2 The Vickers Hardness Values of Water-quenched $Fe_{62}Al_{38}$ Specimens from 800 °C at Different Aging Time

Aging time (h)	0	0.5	1.5	3.5	5.5
Hardness (MPa)	381	377	367	346	323

Conclusions

The hardness of the furnace-cooled Fe-Al alloys increases with increasing Al content when Al content is less than 23 (at.%) Al and then decreases when more than 23 (at.%) Al. The furnace-cooled $Fe_{77}Al_{23}$ alloy has the largest hardness value among all furnace-cooled alloy, which is attributed to the ordered $D0_3$ structure and the effect of solid solution hardening. The effect of quenching on the hardness of the $Fe_{77}Al_{23}$ and $Fe_{71}Al_{29}$ alloys can be obviously observed since they have low thermal vacancy concentration compared with $Fe_{62}Al_{38}$ with B2 structure. The hardness of the $Fe_{62}Al_{38}$ alloy increases obviously with increasing quenching temperature. This increase in hardness is attributed to the strengthening effect of thermal vacancy resulted from quenching. The introduction of thermal vacancy cause lattice constant to reduce and the diffraction angle is shifted to larger angle. The hardening effect resulted from thermal vacancies can be reduced by the ageing at low temperature.

Acknowledgements

This work is sponsored by Qing Lan Project of Jiangsu and supported by research foundation of Suzhou Vocational University (2013SZDYJ05).

References

- [1]H.-E Schaefer, B. Damson, E. Weller, E. Arzt and E. P. George: *phys. stat. sol. (a)* 160 (1997), 531-540.
- [2]H.-E Schaefer, K. Frenner and R. Wurschum: *Phys. Rev. Lett.* 82 (1999), 948-951.
- [3]Y. A. Chang, L. M. Pike, C. T. Liu, A. R. Bilbrey and D. S. Stone: *Intermetallics* 1 (1993), 107-115.
- [4]R. Würschum, C. Grupp and H.-E Schaefer: *Phys. Rev. Lett.* 75 (1995), 97-100.
- [5]O. Dimitrov, in: *Intermetallic Compounds-Principles and Practice*, (ed. J. H. Westbrook et al.), John Wiley, Chichester, Vol.1 (1994), p.771.
- [6]Y. Mishin et al (ed.):*Diffusion Mechanisms in Crystalline Material*, MRS Symposia Proceedings, No.527, Materials Research Society, Pittsburgh (1998).
- [7]G. Sauthoff, in: *Diffusion in Ordered Alloys*, (ed. B. Fultz et al.), TMS, Warrendale (1993), p.205.
- [8]J. Čížek, F. Kukáč, O. Melikhova, I. Procházka, R. Kužel: *Acta Mater.* 59 (2011), 4068-4078.
- [9]M. Zhao, K. Yoshimi, K. Maruyama, K. Yubuta: *Acta Mater.* 64 (2014), 382-390.
- [10]Z. C. Zhou, Z. Y. Gao and F. S. Han: *Journal of Physics: Condensed Matter.*15 (2003), 6809-6815.
- [11]Z. C. Zhou, F. S. Han and Z. Y. Gao: *Acta Mater.* 52 (2004), 4049-4054.
- [12]A. S. Nowick and B. S. Berry: *Anelastic Relaxation in crystalline solids*, New York and London, Academic Press (1972).
- [13]G. Hasemann, J. H. Schneibel, M. Krüger, E. P. George: *Intermetallics* 54 (2014), 95-103.
- [14]O. Kubaschewski: *Iron-Binary Phase Diagrams*, Berlin, Springer-Verlag (1982).
- [15]M. Eggersmann and H. Mehrer: *Phil. Mag. A* 80 (2000), 1219-1244.
- [16]D. G. Morris, M. Leboeuf, S. Gunther and M. Nazmy: *Phil. Mag. A* 70 (1994),1067-1090.
- [17]M. A. Morris, O. George, D. G. Morris: *Mater. Sci. Eng. A* 258 (1998), 99-107.
- [18]M. A. Morris, D. G. Morris: *Scripta Metall.*38 (1998), 509-516.
- [19]R. Jenkins, et al: *Quantitative X-ray Spectrometry*, New York (1979).
- [20]E. P. Bertin: *Principles and Practice of X-ray Spectrometric Analysis*, New York-London, Plenum Press(1975).
- [21]H. P. Klug, L. E. Alexander: *X-ray diffraction procedures for poly-crystalline and amorphous materials*, second edition, New York, John Wiley and Sons, (1974), p.491.