K 1.4003

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Static strain aging of grade 1.4003 ferritic stainless steel was investigated. The test material was pre-strained to 5% elongation under uniaxial tension and subsequently aged at temperatures between 200°C and 300°C. The aging timec unia1T

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Bake-hardening steels are commonly used to manufacture automotive exterior body parts such as roofs, hoods, and door outer panels, i.e., parts that are painted after forming into shape. These steels are designed to achieve a significant increase in yield strength during the low-temperature heat treatment performed to cure the paint. The gain in yield strength produced by the paint baking can range from 30 MPa to 50 MPa. The increased final strength provides improved dent resistance for the car body. Bake-hardening utilizes the phenomenon of strain aging. Strain aging is common in metals having a body-centered cubic structure. The kinetics of the process are controlled by the long-range diffusion of interstitials to the stress field surrounding dislocations. Therefore, the required aging time and temperature depend on the diffusivity of interstitials in the metal. [1]

The grade 1.4003 is unstabilized 12% chromium ferritic stainless steel designed for structural applications. In contrast to many other ferritic stainless steel grades, 1.4003 has the weldability and toughness properties required of structural applications at sub-zero conditions. Grade 1.4003 is often used as cold-formed tubes and profiles to construct lightweight bus body frames. An increased in-service dent and impact resistance would be advantageous in this application.

Since the classical theory of strain aging was developed in the 1940s by Cottrell and Bilby [2], numerous studies

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have been made to static strain aging of low-carbon steel. In contrast, the research on static strain aging in ferritic stainless steels is limited. Buono et al. [3] studied the kinetics of strain aging in unstabilized 16% Cr grade 1.4016 in solution annealed state. The specimens were

C							
C	Si	Mn	P	S	Cr	Ni	N
0.007	0.26	1.41	0.028	0.001	11.3	0.4	0.016

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The testing procedure consisted of four distinct stages. First, standard tensile testing specimens were machined from the test material parallel to the transverse direction. Then, each specimen was prestrained to a 5.0% permanent elongation using a tensile testing machine; the loading rate was 0.00025 1/s. The prestrained specimens were aged at 200°C, 250°C, or 300°C in a laboratory furnace; the soaking time varied between 30 minutes and one week. The heat treatment was followed by air cooling to ambient temperature. During the heat treatments and subsequent cooling, the temperature of each specimen was measured with a K-type thermocouple. The effective soaking time t_s was computed based on the temperature T during heating, soaking, and cooling as follows:

RESULTS

The aging heat treatment restored the pronounced yield point at all aging temperatures; the prestrained, unaged specimens showed continuous yielding. As shown in Figs. 2 and 3, the yield strength ΔY and yield point elongation A_e increased with aging temperature and time. It may also be seen that the increment in the yield stress did not increase after 48.5 hours of aging at T = 300°C. Therefore, it was concluded the aging process was very close to completion in the two most prolonged heat treatments. Hence, the saturation value for the increment in the yield stress produced by the aging process was estimated as 57 MPa.
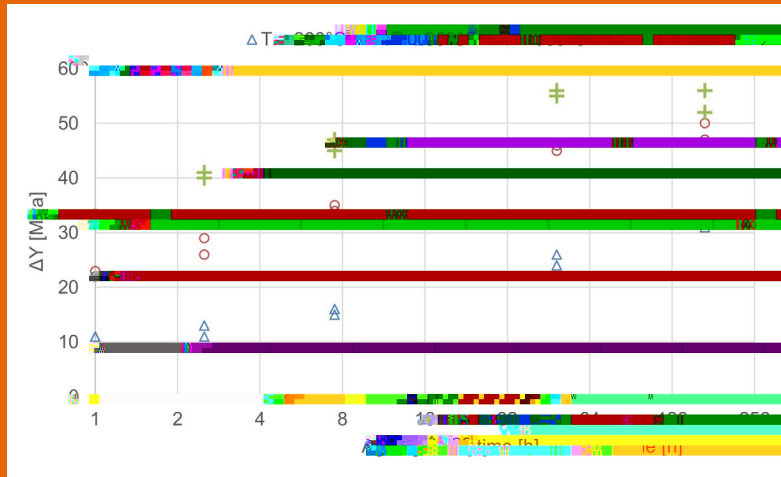

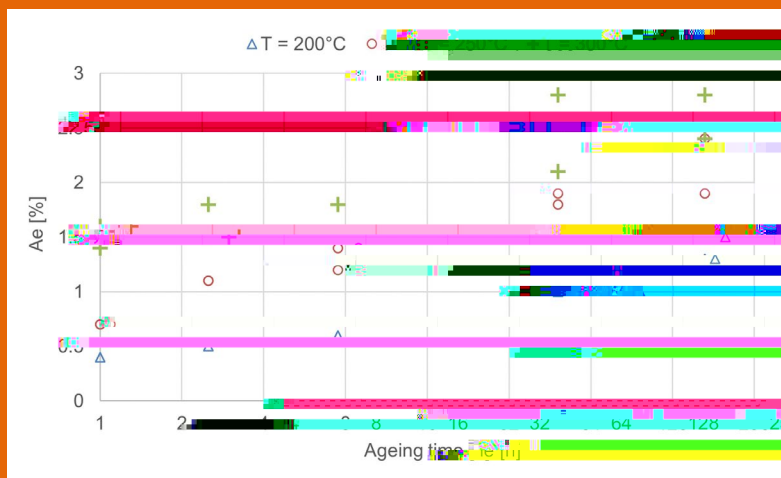**Fig. 2 -** The increment of yield strength, ΔY, caused by isothermal aging.

Fig. 3 - The yield point elongation, Ae, increases with increasing aging temperature and time.

Following ... et al. [3], the aging kinetics was modeled with the Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation

$$W = 1 - \exp[-(kt)^n] \qquad (2)$$

where W is ...ed volume fraction, and t is the aging time. Assuming that the increase in the yield strength is caused by the ...h aging, the volume fraction of aged material can be estimated with

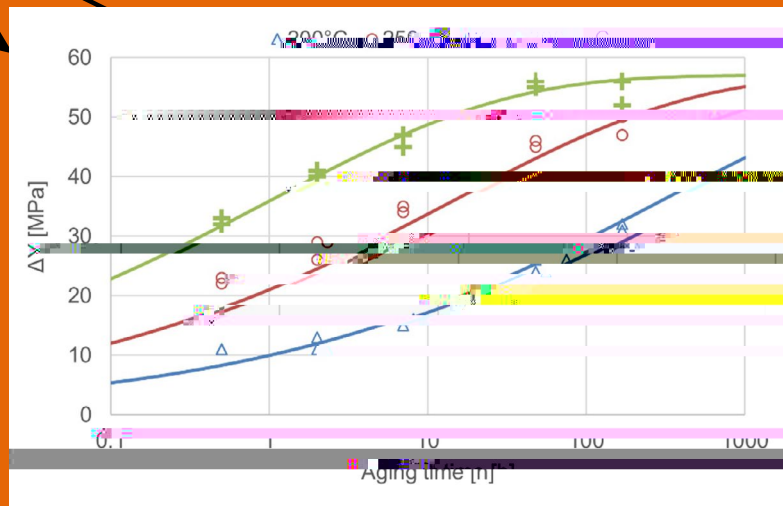$$W = \frac{\Delta Y}{\Delta Y_{max}} \qquad (3)$$

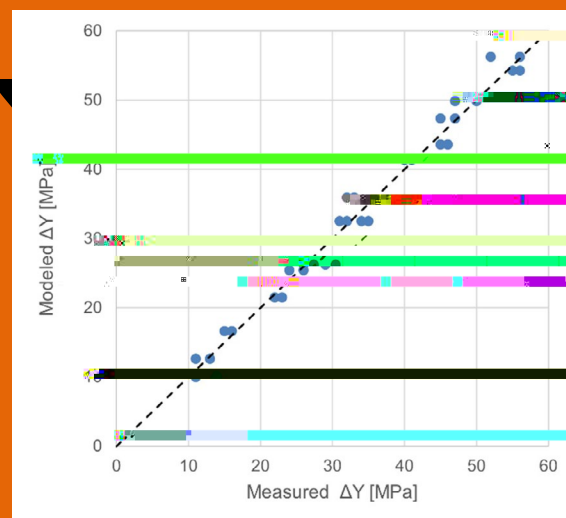**Fig. 5 -** Measured and predicted increment in the yield strength.

. 6 - Correspondence between measure and predicted increment in the yield strength.

DI C IO

Table 4 s a comparison of kinetic parameters obtained in present work and published values for ferritic stee es. The values Harper [9] has reported for pure - re also shown for reference. It may be seen that t ivation energy obtained in the present work is in g greement with those reported elsewhere for ferritic ess steel grades. Golovin et al. [10] determined ctivation energy for diffusion of carbon in high-ch m ferritic steels using internal friction experimen test materials contained 8 to 35 weight percentage omium. The obtained activation energy values increased with increasing chromium content and ranged from 119 kJ/mol to 141 kJ/mol for the 8% and 35% chromium alloys. A parabolic fit to the activation energy values given by Golovin et al. suggests that the activation

energy for the diffusion of carbon in Fe-Cr alloys containing 11.5% and 16.5% chromium would be Q = 122 kJ/mol and Q = 129 kJ/mol, respectively. These values are in excellent agreement with activation energies determined in the present work for 11.5% Cr and that determined by Buono et al. [3] for 16.5% Cr ferritic stainless steels.

The activation energies in Table 4 are significantly higher for ferritic stainless steel grades than for -iron. Golovin et al. [10] argued that chromium atoms produce nonequivalent interstitial positions, thereby increasing the activation energy. This hypothesis was recently questioned by Herschberg et al. [11], who modeled the internal friction and tracer diffusion experiments in ideal Fe-Cr-C alloys using atomistic methods. They used density functional theory (DFT) to calculate the bond energy and energy of migration for carbon atoms. The

calculated values were used to simulate internal friction and tracer diffusion experiments in Fe-Cr-C alloys with 0% and 100% chromium. Their results did not agree with the experimental study of Golovin et al.; the increase in the activation energy for the diffusion of carbon was significantly smaller than that observed by Golovin et al. Therefore, Herschberg et al. suggested that the notable increase in the activation energy observed in the earlier study was produced by the interaction of carbon with defects such as dislocations and vacancies.

An alternative explanation might be proposed based on the work of ermák and Král [12]. They studied the diffusion in carbon-supersaturated ferrite. The test materials included pure -iron and Fe-Cr binary alloy with 15% chromium. In both cases, the diffusion of carbon could be described with the Arrhenius equation. Carbon diffusion was independent of chromium's presence in the matrix; the activation energy for the diffusion of carbon was 158 kJ/mol in both model materials. It was concluded that the carbon atoms diffuse in ordered structures rather than individual atoms in the supersaturated matrix. This conclusion is supported by Kabir et al. [13], who studied the diffusion in the Fe-C system using density functional theory. They concluded that complexes containing one vacancy and two carbon atoms are abundant in carbon-rich ferrite. These complexes are immobile. The calculated binding energy of this vacancy cluster was 1.46 eV, i.e., 0.73 eV/atom (70 kJ/mol). The activation energy associated with the transference of carbon atoms from the cluster to the locations around dislocations should be equal to the sum of the binding energy of the cluster molecule and the activation energy for the diffusion of carbon atoms, i.e., 154 kJ/mol. This value agrees with the activation energy obtained by ermák and Král [12] for supersaturated ferrite.

The activation energy for aging in different ferritic stainless steel grades is, without exception, significantly higher than the values reported for -iron. The presence of chromium atoms does not considerably increase the activation energy of carbon diffusion in ferrite [11,12], whereas the carbon diffusion is slowed down in the carbon-supersaturated ferrite [12]. Therefore, the most likely reason for the higher activation energy in ferritic stainless steels is that the ferrite is supersaturated with carbon at aging temperatures. In pure -iron, ferrite is in equilibrium with cementite (Fe_3C), whereas in ferritic stainless steel, the equilibrium carbide is $Cr_{23}C_6$. Cementite precipitation is expected to be considerably faster than chromium carbide since the former does not require diffusion of substitutional Cr atoms. The activation energy for bulk diffusion of chromium in ferrite is high, 250 kJ/mol [14]. Therefore, the precipitation of cementite will be faster than that of the chromium carbide when the steel strip is cooled after final annealing in a continuous annealing line. It is also possible that the chromium alloying reduces the solubility of carbon in ferrite. In this case, a considerably smaller concentration of carbon atoms will produce a supersaturated ferrite.

In the original theory for static strain aging in low-carbon steels by Cottrell and Bilby [2], the time exponent equals n = 2/3. As discussed by Lement and Cohen [15], this particular value is related to the assumption that the depletion of carbon atoms occurs in a cylindrical volume surrounding randomly situated dislocation lines. By assuming that the dislocations are arranged in cell walls, as they usually are in ferritic stainless steels and other metals with high stacking-fault energy, the geometry of carbon flow is changed from two-dimensional to one-dimensional and the time exponent is reduced to n = 1/3. The time exponent obtained in the present study, n = 0.29, is close to Lement and Cohen's theoretical value.

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Tab. 4 - Comparison of activation energy and time exponent values.

Kinetic model parameters					
	Material				Ref.
0.29	This work	Unstabilized 16.5% Cr ferritic stainless steel 1.4016		128 $\frac{kJ}{mol}$	
...ic stainless steel 1.4016	127 $\frac{kJ}{mol}$	0.36 – 0.47	[3]	Unstabilized 16.5% Cr ferriti...	

SUMMARY AND CONCLUSION

Our results show that low chromium ferritic stainless steel grade 1.4003 is susceptible to strain aging. The aging heat treatment restored the pronounced yield point at all aging temperatures. Furthermore, the yield strength and yield point extension increased with increasing aging temperature and time. The apparent activation energy of the process was 128 kJ/mol. While this value is considerably higher than the typical value of about 80 kJ/mol for C-in-used for bake hardenable low-carbon steels, it agrees with the literature value for interstitial diffusion in high-chromium Fe-Cr alloys determined with internal friction measurements. The strength increments are comparable to bake-hardenable low-carbon steels used in the automotive industry. The increments were, however, relatively modest compared to the relatively high yield strength of the cold-worked material. Furthermore, a long soaking time at a relatively high temperature was needed to achieve the highest improvements in the mechanical properties. Therefore, the processing costs may be too high compared to the modest strength increment produced.

REFERENCES

[1] Baker L, Parker S, Parker J. Metallurgy and processing of ultralow carbon bake hardening steels. Materials Science and Technology. 2002;...:368.

[2] Cottrell AH, Bilby BA. Dislocation theory of yielding and strain ageing of iron. Proceedings of the Physical Society Section A. 1949;...

[3] Buono V, Gonzalez B, Andrade M. Strain aging of AISI 430 ferritic stainless steel. Scripta materialia. 1997;38:185–190.

[4] Kaçar R, Gündüz S. Increasing the strength of AISI 430 ferritic stainless steel by static strain ageing. Kovove Mater. 2009;47:185–191.

[5] Palosaari M, Manninen T. Bake-hardening of stabilized ferritic stainless steels. Special Edition of Steel Research International for Metal Forming 2012, Wiley-VCH Verlag GmbH. 2012;951–954. Available from https://onlinelibrary.wiley.com/page/journal/1869344x/homepage/metal-forming-2012.html

[6] Fu Z. Study of Static Strain Aging of Selected Ferritic Steels. Master's thesis. Tampere University of Technology; 2017.

[7] Fu Z, Kotilainen H, Manninen T, Peura P. Bake Hardening Behavior of 1.4003 Ferritic Stainless Steel. Ohutlevy. 2017:28–33.

[8] Alvarez J, Sotomayor A, Herrera E. Permanent elimination of the yield-point phenomenon in AISI 430 stainless steel by skin-pass rolling. Journal of materials science. 1994;29:5833–5838.

[9] Harper S. Precipitation of carbon and nitrogen in cold-worked alpha-iron. Physical review. 1951;83:709.

[10] Golovin IS, Sarrak VI, Suvorova SO. Influence of carbon and nitrogen on solid solution decay. Metallurgical transactions A. 1992;...–2579.

[11] Hersom R, Fu C-C, Nastar M, et al. Atomistic modelling of the diffusion of C in FeCr alloys. Acta Materialia. 2019;165:638–653.

[12] Jernkvist L. Extremely slow carbon diffusion in carbon-supersaturated surface of ferrite. Kovove Mater. 2014;52:125–133.

[13] Kabir M, Lau TT, Lin X, et al. Effects of vacancy-solute clusters on diffusivity in metastable Fe-C alloys. Physical Review B. 2010;...4112.

[14] Bowen AW, Leak GM. Solute diffusion in alpha-and gamma-iron. Metallurgical Transactions. 1970;1:1695–1700.

[15] Lement B, Cohen M. A dislocation-attraction model for the first stage of tempering. Acta Metallurgica. 1956;4:469–476.

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