Transactions of the Materials Research Society of Japan 29 [8] 3465-3468 (2004)

Thermal Expansion of the Mullite Fiber / High-speed Steel Composite

Taro Nakazono, Soichiro Sameshima and Yoshihiro Hirata
Department of Advanced Nanostructured Materials Science and Technology,
Graduate School of Science and Engineering, Kagoshima University
1-21-40 Korimoto, Kagoshima 890-0065, Japan
Fax: 81-99-257-4742, e-mail: hirata@apc.kagoshima-u.ac.jp

The high-speed steel (HSS) consisting of Fe and several kinds of transition metal carbides has a high fracture toughness and high hardness. In this experiment, mullite long fibers with a high tensile strength and a low coefficient of thermal expansion were incorporated into HSS matrix to increase the hardness, strength, fracture toughness and thermal shock resistance. Monolithic HSS showed a change of thermal expansion associated with the phase transition from γ-Fe + Fe_3C to γ-Fe at 1087 K during a heating process in an Ar atmosphere. The γ-Fe + Fe_3C $\rightarrow$ α-Fe + Fe_3C phase transition temperature during a cooling process was measured at 600 - 1020 K, depending on the cooling rate of HSS. The incorporation of 15 - 30 vol% mullite fabric (85 mass% Al_2O_3+15 mass% SiO_2) decreased the γ-Fe + Fe_3C $\rightarrow$ γ- Fe phase transition temperature during the heating process and was effective to decrease the coefficient of thermal expansion. The experimentally determined coefficient of thermal expansion was compared with the theoretically calculated coefficient of thermal expansion.

Key words: High-speed steel, Mullite fiber, Composite, Thermal expansion

1. INTRODUCTION

The high - speed steel (HSS) consisting of Fe and several kinds of transition metal carbides has a high fracture toughness (25-28 MPa • $m^{1/2}$) and high hardness (7.5 GPa in Vickers hardness) [1, 2] . This material is applied to cutting tool or wear – resistant materials. The use of HSS experiences relatively high thermal shock, because a coolant such as water or oil is flowed over the surface of heated HSS. To overcome the high thermal shock, a high strength is needed for HSS. The purpose of this research is to increase the hardness, strength, fracture toughness and thermal shock resistance of HSS. A possible strategy is to incorporate a hard ceramic material with high strength in HSS matrix. The fracture toughness ($K_{IC} = (2\,E\gamma)^{1/2}$) of HSS increases with the addition of ceramic material with a high Young's modulus (E) and by the introduction of fracture energy adsorption mechanisms providing the increase of fracture energy (γ). The critical temperature difference (ΔTc) to no crack formation for brittle materials is expressed by $\Delta Tc = \sigma(1 - \nu) / \alpha E$, where σ is the tensile strength, ν the Poisson ratio, α the coefficient of thermal expansion, and E the Young's modulus [3] . A higher Young's modulus and a lower coefficient of thermal expansion of ceramic material compared with the properties of HSS provide the opposite influence on the thermal shock resistance of composite. When the product of αE becomes lower in the ceramics / HSS composite, the thermal shock resistance of HSS may be improved. The typical values of $\alpha = 3.5 \times 10^{-6}\ K^{-1}$ [4] and E = 210 GPa for mullite provide the product of $\alpha E = 7.35 \times 10^{-4}$ GPa • K^{-1}. On the other hand, the product of αE for HSS is calculated to be 3.12×10^{-3} GPa •K^{-1} ($\alpha = 13 \times 10^{-6}\ K^{-1}$, E = 240 GPa). The above calculation suggests a possibility of increased thermal shock resistance with addition of mullite fiber to HSS. Furthermore, substitution of the typical values for mullite fiber, σ = 1.7 - 2.2 GPa, ν =0.27, $\alpha = 3.5 \times 10^{-6}\ K^{-1}$ and E = 210 GPa into the equation of critical temperature difference leads to ΔTc = 1688 - 2185 K, supporting the high thermal shock resistance. In this study, the coefficient of thermal expansion for mullite fiber / HSS composite was measured at 300 - 1273 K in an Ar atmosphere to increase the thermal shock resistance of the composite.

2. EXPERIMENTAL PROCEDURE

A high - speed steel powder (Mitsubishi Steel Mfg. Co., Ltd., Japan) has a cumulative particle size distribution of 4.43 μm / 10 %, 11.23 μm / 50 % and 24.93 μm / 90 % and a following chemical composition (mass %): 81.91 Fe, 0.85 C, 4.03 Cr, 1.94 V, 4.88 Mo, and 6.01 W. The true density measured with the pycnometer using kerosine was 7.931 g / cm^3. Monolithic HSS powder in carbon mold was heated to 1323 K at 10 K / min and pressed by carbon die under a pressure of 39 MPa for 2 h in an Ar atmosphere (FVH – 5 type, Fuji Denpa Kogyo Co., Japan) [5]. The mullite fiber of an average diameter of 10 μm (Sumitomo Chemical Co., Ltd., Japan) has a chemical composition of 85 mass % Al_2O_3 and 15 mass % SiO_2 (1000 filament / yarn). The true density of the fiber was 3.226 g / cm^3. The tensile strength and tensile modulus at room temperature are reported by the supplier to be 2.0 GPa and 210 GPa, respectively. The mullite woven fabrics with sizes of 38 mm length, 25 mm width and 200 μm thickness were laminated together in an ethylenglycol suspension containing 40 vol % HSS powder in a stainless steel box. Ultrasonic irradiation of 38 kHz was applied to penetrate the HSS powder into the mullite fabric [6]. The fiber fraction of the composite was adjusted to be 15 and 30 vol %. The dried green composite was heated to 1073 K at 5 K / min and pressed by carbon die under a pressure of at 39 MPa. The pressed composite was heated to 1473 K at 10 K / min and sintered for 5 min to infiltrate the HSS into the open spaces of the slica-alumina fabric. The infiltrated HSS was sintered at 1373 K for 2 h in an Ar atmosphere to suppress the grain growth of HSS and the degradation of the fabric. The hot-pressed sample was cut into test specimen 10 mm long, 4 mm wide and 3 - 5 mm thick and polished with diamond paste of 1 μm. The microstructures of the hot-pressed monolithic HSS and composites were observed by scanning electron microscopy (SM-300, Topcon Co., Japan). The thermal expansion of the polished samples was measured by thermal mechanical analyzer (Thermoplus series 8310, Rigaku Co., Japan) in an Ar atmosphere. The measured thermal expansion data were calibrated by blank test and the reference data of α-alumina.

3. RESULTS AND DISCUSSION

3.1 Thermal expansion of monolithic HSS

The hot-pressed HSS was sintered to a density higher than 99 % of theoretical density. α -Fe and Fe_3C were identified in the x-ray diffraction pattern of the hot-pressed HSS. The microstructure of high-speed steel (HSS) contained dispersed white grains of 0.3-1.6 μm size, corresponding to the transition metal carbides such as Fe_3C, VC, WC, Mo_2C and Cr_2C_2. This microstructure represents the fine transition metal carbide particles-reinforced α-Fe matrix composites.

Figure 1 shows the thermal expansion of the monolithic HSS during the heating and cooling processes at rates of (a) 3 K/min and (b) 10 K/min. Change in the thermal expansion was observed at 1087 and 1020 K in the heating and cooling processes, respectively, at a rate of 3 K/min. Increase in the heating and cooling rates of HSS to 10 K/min caused (1) the significant decrease of the temperature giving the change in the thermal expansion in the cooling process and (2) the decreased reproducibility of experimental results. From the chemical composition of HSS, the fractions of Fe and C become 98.97 and 1.03 mass % in the two component system. According to the phase diagram of the Fe-C system [7] at 1 mass% C, a transition from α-Fe + Fe_3C to γ-Fe + Fe_3C occurs at 996 K in the heating process. Furthermore, γ-Fe + Fe_3C phases change to γ-Fe at 1073 K during the heating. The above phase transition is accompanied by the following volume change because of the difference of density between α- Fe (7.874 g/cm^3) [8] and γ-Fe (8.000 g/cm^3) [9] : (1) α-Fe + Fe_3C → γ-Fe + Fe_3C, - 1.8 % (shrinkage), (2) γ-Fe + Fe_3C → γ-Fe, - 0.16 % (shrinkage). These volume changes correspond to the linear shrinkage of 0.60 and 0.05 % for the above cases (1) and (2), respectively. The measured linear shrinkage and expansion in heating and cooling processes was 0.19 and 0.17 %, respectively.

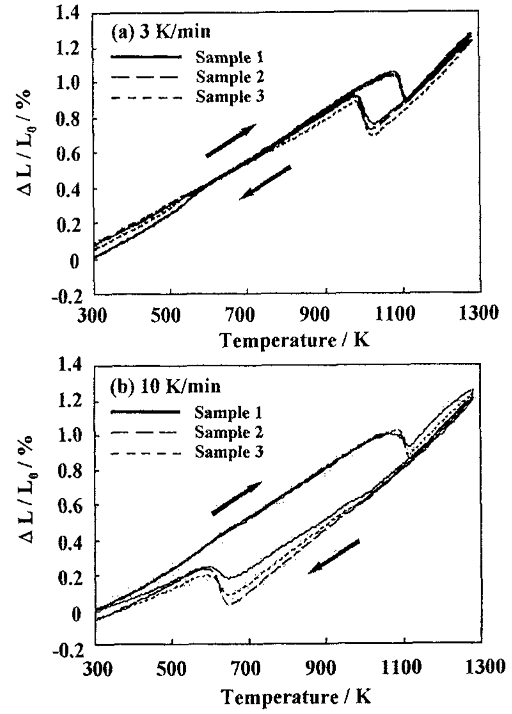

Fig. 1 Thermal expansion of monolithic HSS heated and cooled at a rate of (a) 3 K/min and (b) 10 K/min.

The comparison between the above calculation and the measured change of the thermal expansion of HSS suggests the following conclusions: (1) The decrease of thermal expansion at 1087 K measured in the heating process of HSS at 3 K/min, corresponds to the volume shrinkage from γ-Fe + Fe_3C to γ-Fe. This phase transition proceeds rapidly, because the measured phase transition temperature was almost independent of the heating rates (3-20 K/min). In the heating process, it was difficult to detect the phase transition from α-Fe + Fe_3C to γ-Fe + Fe_3C in the thermal expansion measurement. (2) The sudden increase of thermal expansion, measured at 1020 K in the cooling process of HSS at 3 K/min, represents the phase change from γ-Fe + Fe_3C to α-Fe + Fe_3C. This phase transition proceeds slowly, because the transition temperature shifted to the lower value when the cooling rate was increased. In the cooling process, it was difficult to measure the phase change from γ-Fe to γ-Fe + Fe_3C in the thermal expansion measurement.

The thermal expansion of monolithic HSS heated and

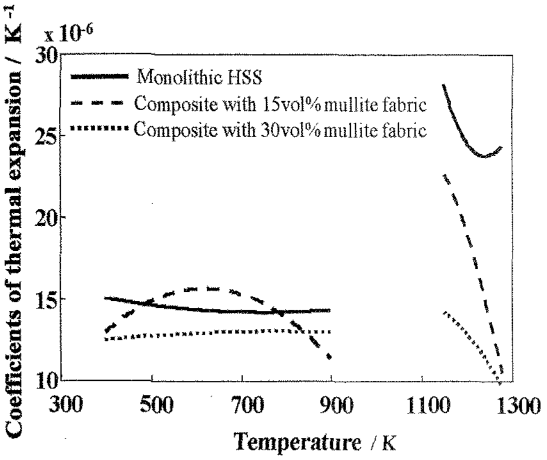

Fig. 2 Coefficients of thermal expansion of monolithic HSS and the HSS composites with 15 and 30 vol % mullite fabric in the temperature range from 400 to 900 K and from 1150 to 1273 K.

cooled at 3 K/min was approximated by Eq.(1),

$$\frac{\Delta L}{L_0} = c_1 + c_2 T + c_3 T^2 + c_4 T^3 \qquad (1)$$

where c_1, c_2, c_3 and c_4 are the experimental constants, and T the temperature (K). The coefficient of thermal expansion (CTE), α, was determined by differentiating Eq. (1) with respect to T (Eq. (2)) [10]

$$\alpha = \frac{1}{L_0}\left(\frac{dL}{dT}\right) = c_2 + 2c_3 T + 3c_4 T^2 \qquad (2)$$

Figure 2 shows the α value of monolithic HSS heated at 3 K/min as a function of heating temperature. The α value for α-Fe + Fe_3C (400-900 K) was in the range from 14.2 x10^{-6} to 15.0 x10^{-6} K^{-1}.On the other hand, the α value for γ-Fe (1150-1273 K) was in the range from 23.7 x10^{-6} to 28.2 x10^{-6} K^{-1}.

3.2 Thermal expansion of mullite fabric / HSS composites

The composites with 15 and 30 vol % mullite fabric were densified to 96.4 and 98.2 % of theoretical density, respectively. Figure 3 shows the cross section of the composite with 30 vol% mullite yarn. The HSS penetration into the mullite yarn without the sintering of mullite fibers.

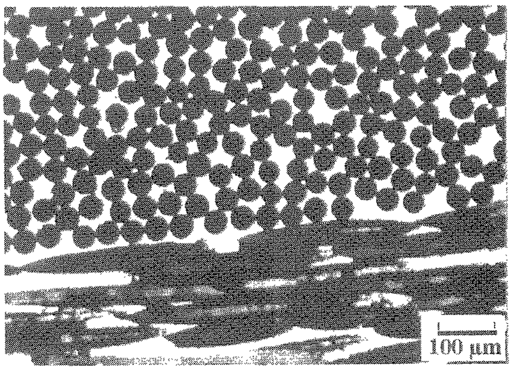

Fig. 3 Cross sections of the HSS composites with 30 vol% mullite fabric.

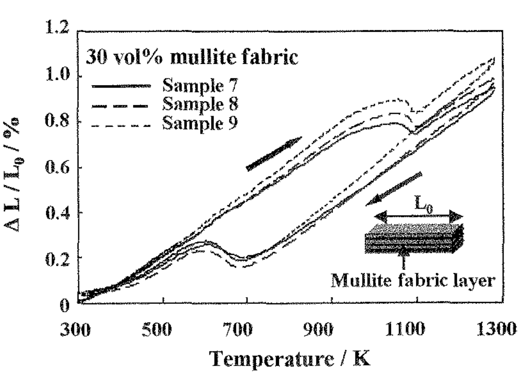

Fig. 4 Thermal expansion of mullite fabric / HSS composites with (a) 15 vol% and (b) 30 vol% mullite fabric, measured at 10 K/min.

Figure 4 shows the thermal expansion of layered HSS composites with 30 vol% mullite fabric, heated and cooled at 10 K/min. The measurement was carried out along the direction parallel to the layered mullite fabric. In the composite, the decreased thermal expansion was measured in the temperature range from 936 to 1065 K, corresponding to the phase transition from α-Fe + Fe_3C to γ-Fe + Fe_3C. Further heating resulted in the phase transition to γ-Fe phase from γ-Fe + Fe_3C at 1100 K. In the cooling process, the phase transition of γ-Fe + Fe_3C to α-Fe + Fe_3C was measured at 688 K. The above results apparently indicate that the addition of mullite fabric with a lower CTE (~ 3.5x10^{-6} K^{-1}) to HSS decreases the phase transition temperature for γ-Fe + $Fe_3C \rightarrow$ γ-Fe in the heating process and also increases the phase transition temperature for γ-Fe + $Fe_3C \rightarrow$ α-Fe + Fe_3C in the cooling process.

The α value by Eq.(2) for the composites are shown in Fig.2. Addition of mullite fabric of 15-30 vol% to HSS was effective to decrease the coefficients of thermal expansion of γ-Fe (T>1150 K) of HSS. When HSS composite bonded with horizontal mullite layer (volume fraction , V_f) is cooled from a high temperature (T_1) to room temperature (T_2) [14], the net tensile stress (σ_m) of HSS matrix of volume faction V_m is equal to the net compressive stress (σ_f) of mullite layer , as expressed by Eq.(3) .

$$\sigma_m V_m + \sigma_f V_f = 0 \qquad (3)$$

The σ_m and σ_f are given by Eqs.(4) and (5), respectively,

$$\sigma_m = \left(\frac{E_m}{1-\nu_m}\right)\Delta T\left(\alpha_c - \alpha_m\right) \qquad (4)$$

$$\sigma_f = \left(\frac{E_f}{1-\nu_f}\right)\Delta T\left(\alpha_c - \alpha_f\right) \qquad (5)$$

where m, f and c correspond HSS, mullite layer and composite, respectively, and ΔT is equal to the temperature difference of (T_1-T_2). Substitution of Eqs.(4) and (5) into Eq.(3) yields Eq.(6) giving the influence of horizontal mullite layer on the CTE of the layered composite.

$$\alpha_c = \frac{\alpha_m V_m\left(\frac{E_m}{1-\nu_m}\right) + \alpha_f V_f\left(\frac{E_f}{1-\nu_f}\right)}{V_m\left(\frac{E_m}{1-\nu_m}\right) + V_f\left(\frac{E_f}{1-\nu_f}\right)} \qquad (6)$$

Figure 5 shows the calculated α_c for the values of E_m= 240 GPa, ν_m= 0.27, E_f= 210 GPa and ν_f= 0.27 .The α_m and α_f (3.5 x 10^{-6} K^{-1}) values, at 700, 900 and 1200 K were obtained from Fig.2 and Reference 4, respectively. The calculated α_c decreases with increasing volume fraction of mullite layer. The experimental α_c values for the composite with 30 vol % mullite fabric were higher than the calculated values. However the composite contained 15 vol% longitudinal and 15 vol % horizontal mullite fibers. When the measured α values were plotted to 15 vol% mullite fiber content, the difference of α_c values between the calculation and experiment becomes significantly small, suggesting the small influence of longitudinal fiber on the α_c values.

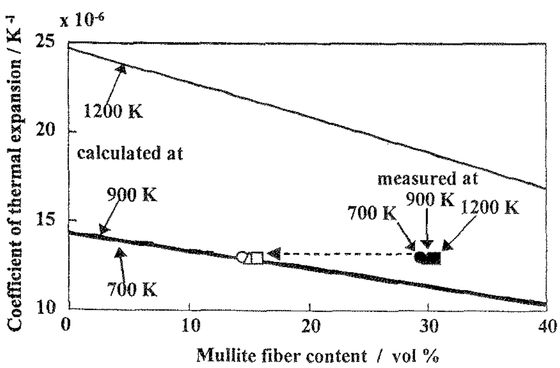

Fig.5 Coefficients of thermal expansion at 700-1200 K for the mullite fabric / HSS laminated composite as a function of fiber content.

4. Conclusions

Monolithic HSS showed a decrease of thermal expansion at 1087 K associated with the phase transition from γ-Fe + Fe_3C to γ- Fe during the heating process. This phase transition proceeded rapidly and was independent of heating rate. The phase transition temperature (1020 K) from γ-Fe + Fe_3C to α-Fe + Fe_3C during the cooling process decreased with increasing cooling rate. Coefficient of thermal expansion (CTE) of HSS was in the range from 14.2 x 10^{-6} to 15.0 x 10^{-6} K^{-1} at 300-900 K, and 23.7x 10^{-6} - 28.2 x 10^{-6} K^{-1} at temperatures above 1150 K. The incorporation of 15 - 30 vol% mullite fabric decreased the phase transition temperature of γ-Fe + Fe_3C → α- Fe during the heating process and was effective to decrease the CTE of HSS. The measured CTE of laminated composite with 30 vol% mullite fabric was close to the calculated CTE value using the volume fraction of horizontal mullite layer.

References

[1] A. Hirano, H. Nakayama, J. Funakoshi, H. Okano and A. Kosaka, J. Soc. Mat. Sci., Japan, 46, 1161 – 1166 (1997).

[2] A. Suzuki, in "Kinzokubinran (Metal Hand Book)", Edited by The Japan Institute of Metals, Maruzen, Tokyo (1976) p. 790.

[3] W. D. Kingery, H. K. Bowen and D. R. Uhlmann, in "Introduction to Ceramics", John Wiley & Sons, 2 nd ed. New York (1976) pp.816-822.

[4] H. Katsuki, A. Kawahara, H. Ichinose, S. Furuta and S. Yoshida, J.Ceram.Soc.Jpn.,97, 1521-1524 (1989).

[5] Y. Hirata, Y. Nakashima, Y. Niibo, S. Sameshima, S. Uchida, S. Hamauzu and S. Kurita, in Proceedings of the Symposium on Refractories for the Next Millennium-The Ninth Symposium Refractories for the Alumina Industry, The American Ceramic Society Pacific Caost Regional Basic Science Division and Electronics Division Meeting, Bellevue, published by The Minerals Metals and Materials Society, Edited by G.Opera, Bellevne, WA, USA, 2000, pp.95-108.

[6] Y. Niibo, K. Yuchi, S. Sameshima and Y. Hirata, J.Ceram.Proc. Res., 1, 83-87 (2000)

[7] Alloy Phase Diagrams, Vol.3 in American Society for Metals, Edited by H. Baker, ASM International, Ohio (1992), Index 2.110.

[8] ICDD (International Centre for Diffraction Data) No. 6-696.

[9] ICDD (International Centre for Diffraction Data) No. 31-619

[10] S. Sameshima, M. Kawaminami and Y. Hirata, J.Ceram.Soc.Jpn.,110, 597-600(2002).

[11] W. D. Kingery, H. K. Bowen and D. R. Uhlmann, in "Introduction to Ceramics", John Wiley & Sons, 2 nd ed., New York(1976) pp.197-200.

(Received December 1, 2003; Accepted June 23, 2004)