Mechanical properties of LaFe$_{11.5}$Si$_{1.5}$/Cu negative thermal composite and its application as clamp materials for tensile test at cryogenic temperatures

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Abstract. La (Fe, Si)$_{13}$ compounds have been widely studied for their excellent negative thermal expansion (NTE) properties. However, their poor mechanical properties limit their practical applications. In this work, LaFe$_{11.5}$Si$_{1.5}$/Cu material was fabricated. It was found that the NTE behavior occurs obviously at cryogenic temperatures and the ratio of $\Delta L/L$ can reach to 0.12%. Mechanical tests indicated that the absolute value of compressive strength at 77K and 300K is 365MPa and 222MPa, respectively. The elastic modulus at 77K and 300K is -109GPa and -87GPa, respectively. In addition, the average hardness is 337Hv performed in the Vickers hardness tester. Loose between the samples and clamps in the tensile test due to the contraction of clamp at low temperatures remains a big issue. In order to solve this problem, some LaFe$_{11.5}$Si$_{1.5}$/Cu NTE sheets are added between the clamp and the tested samples. Results showed that the samples with NTE materials sheets embedded is held tighter by the clamp. The maximum force of the tensile test is 9.77N and 5.48N, respectively, which illustrates that the adding of NTE material does make sense.

1. Introduction

In common sense, the volume of most materials can be changed through temperature shift, obeying a principle of metal expanding on heating and contracting on cooling, which is so-called normal thermal expansion. However, this property easily leads to fatal error in cryogenic environment, especially in aerospace, precision instrument, mechanical device and cryogenic engineering. In late 19th Century, abnormal thermal expansion material was first found by Guillaume$^{[1]}$. Invar, with the constitution of Ni, Fe and few C, its coefficient of thermal expansion (CTE) is very low and expand hardly with the change of temperature. In 1951, Hummel found that the crystalline aggregate of $\beta$-eucryptite, while in an environment
over 1000°C, it contacts with temperature increasing\textsuperscript{[2]}. This abnormal phenomenon is called negative thermal expansion (NTE).

Until now, some materials with excellent NTE properties have been successfully fabricated and tested, such as ZrW\textsubscript{2}O\textsubscript{8}\textsuperscript{[3, 4]}, PbTiO\textsubscript{3}\textsuperscript{[5]}, ScF\textsubscript{3}\textsuperscript{[6, 7]}, antiperovskite manganese nitride\textsuperscript{[8, 9]} and La(Fe, Si)\textsubscript{13}-based compounds\textsuperscript{[10]}. Cubic La(Fe, Si)\textsubscript{13}-based compounds, as one of the typical magnetic refrigeration materials, have been deeply studied by researchers\textsuperscript{[11-13]}, which exhibit large, isotropic and nonhysteretic NTE properties as well. Researches also showed that, by changing the amount of Si, doping other elements into \(\text{La(Fe, Si)}_{13}\)-based compounds, better NTE properties can be achieved\textsuperscript{[14]}.

Though NTE materials have been optimized, the mechanical properties of most NTE materials have not be considered thoroughly for fragile materials easily break in low temperature environment, the clamp used in the tensile test easily loose due to its contraction at cold temperature material. However, in low temperature environment, the clamp used in the tensile test easily loose due to its contraction at cold temperatures, which makes the test results inaccurate. To solve this problem, NTE materials were considered to be added on the sample. Its good property—expanding at cold environment is expected to make the sample held tighter when the temperature descends.

In the previous study, Wang et al.\textsuperscript{[14]} had tested the NTE properties of LaFe\textsubscript{13-x}Si\textsubscript{x} (x=1.5, 1.8, 2.1 and 2.4) and found that LaFe\textsubscript{11.5}Si\textsubscript{1.5} possess the biggest absolute value of average CTE \((-5.6 \times 10^{-6} \text{K}^{-1})\). In our work, 20 wt.% of Cu powder was added into LaFe\textsubscript{11.5}Si\textsubscript{1.5}. Its mechanical properties have been studied and this material is placed high hopes on to improve clamp’s performance in cryogenic environment.

2. Experiment

2.1. Synthesis of material
Polycrystalline samples of LaFe\textsubscript{11.5}Si\textsubscript{1.5} were prepared in an arc-melting furnace under a high-purity argon atmosphere. The purity of La, Fe and Si raw material are all greater than or equal to 99.9%. In order to ensure well heat distribution of these sample, button-shaped sample were smelted four times and each time they were turned over. The arc-melted ingots wrapped by Ta foils were sealed in a quartz tube filled with high-purity argon gas, then homogenized at 1050°C for 20 days, and finally quenched into cold water.

The LaFe\textsubscript{11.5}Si\textsubscript{1.5} particles were pulverized in an agate mortar and mixed with 20% Cu powder. Then the sample were sintered spark plasma sintering(SPS) by furnace (Syntex Lab; SPS Syntex Inc.) at 700°C and 50MPa pressure under vacuum and pressure was held for 5 minutes. The photo of LaFe\textsubscript{11.5}Si\textsubscript{1.5}/Cu composites are shown in figure 1. (a).

2.2. NTE and mechanical property measurement
The linear thermal expansion data(ΔL/L) were measured using a strain gauge over a temperature range of 77-300K. During the process, the Zerodur glass ceramic, whose
coefficient of thermal expansion is near zero, was used for reference. The compressive strength and modulus of elasticity were measured by MTS (CMT 5000) universal material testing machine. Two samples, whose size is 3.2×3.61×10 mm³ (1# sample) and 2.9×3.61×10 mm³ (2# sample) respectively, were tested at 77 K and 300 K. Hardness of the material was tested by automatic rotating Vickers hardness tester.

2.3. Tensile test with carbon fibre plate
The tested sample in tensile test was carbon fibre plate with the size of 155×7×1.8 mm³. Two pieces of Al sheet were adhered on both side of the carbon fibre plate in order to sustain the tested sample, as is shown in Figure 1. (b). LaFe₁₁.₅Si₁.₅/Cu NTE materials, were adhered on the upper side of one Cu sheet. The size of the two Al sheets and LaFe₁₁.₅Si₁.₅/Cu NTE materials is 17×7×3 mm³ and 17×7×1.5 mm³, respectively. In the control experiment, the places of NTE materials were substituted by Cu sheets. D-W glue was used to stick these sheets and plate together. The adhesive order is shown in Figure 1. (c).

MTS-SANS (CMT 5105) universal testing machine with a load capacity of 10kN was used in the tensile test. During tensile test at 77K, the samples and fixtures were immersed in liquid nitrogen. Tensile tests were conducted in displacement control with a stain rate of 10×10⁻⁴ s⁻¹. Samples were fixed by 304 LN stainless steel homemade clamp.

![Figure 1. Photos and diagrams of the tested samples](image)

3. Results and discussion

3.1. Abnormal thermal expansion properties
Figure 2 shows the linear thermal expansion $\Delta L/L$ data (reference temperature: 300 K) as a function of temperature for LaFe$_{11.5}$Si$_{1.5}$/Cu composites in the temperature range from 77 K to 300 K. It can be found that the material presents positive thermal expansion behavior (PTE) from 200 K to 300 K and shows evident NTE behavior in the temperature range of 160 K to 215 K. It can be calculated that the CTE of the composite is $-40.06 \times 10^{-6}$ K$^{-1}$. From room temperature zone to low temperature zone (<180 K), the strain value of the material is more than 1400 ppm and presents remarkable NTE properties.

Figure 2. Temperature dependence of linear thermal expansion $\Delta L/L$ (reference temperature: 300 K) from 77 K to 300 K for LaFe$_{11.5}$Si$_{1.5}$/Cu composites.

### 3.2. Mechanical properties

To evaluate the compressive properties of low-temperature NTE material LaFe$_{11.5}$Si$_{1.5}$/Cu, compression tests were carried out at nitrogen temperature (77 K) and room temperature (300 K). Stress-displacement curves and stress-strain data are obtained from the tests and are used to determine the compressive strength and modulus.

Figure 3 shows the typical compression stress-displacement curves for LaFe$_{11.5}$Si$_{1.5}$/Cu at 77 K and 300 K, respectively. The values of compressive strength are 365 MPa and 222 MPa,
It is found that the compressive strength of the material is much better at cryogenic temperatures than that at room temperatures, which illustrates that the material can maintain its shape to a great extent without too much deformation when compressed in cold environment.

Figure 4. Stress-strain curve of the sample at 77 K and 300 K

Figure 4. shows the stress-strain data for LaFe_{11.5}Si_{1.5}/Cu at 77 K and 300K. From the stress-strain data, the Young’s modulus at each temperature was calculated. They are -109.18 GPa and -87.34 GPa, at 77 K and 300 K, respectively. Since Young’s modulus reflects the rigidity of material, the higher the absolute value is, the more impossible the material deform while traction. The absolute value of Young’s modulus at 77 K is relatively higher than that at 300 K means that it has better mechanical property at cryogenic temperatures. Table 1. shows the hardness test results. The average value of Vickers hardness is 337.7 HV.

Table 1. Results of hardness test

| Test Number | 1   | 2   | 3   | 4   | 5   | Average Value |
|-------------|-----|-----|-----|-----|-----|---------------|
| Vickers hardness (Hv 0.5/10) | 261.9 | 370.9 | 381.5 | 378.4 | 295.7 | 337.7 |

3.3. Tensile test
Figure 5. Force-displacement curve of carbon fibre reinforced epoxy based composite sample by traditional fixture clamp and NTE material embedded sample in the tensile test.

Figure 5. clearly describes the mechanical state of the samples in the tensile test. During the test, the sample was slowly extended by the testing machine, gradually the force reached the maximum value. Then the sample slipped with the force decreasing quickly before the sample were held firmly again by the machine. Next the force began to increase. The whole process repeated several times until the sample finally pulled off by the machine. From Table 2., the results of the tensile test clearly show that, after adding LaFe$_{11.5}$Si$_{1.5}$/Cu NTE material on both side of the carbon fibre plate, the max force is 9.77 kN, which is about 78% more than that of traditional fixture clamp. Also, the tensile strength of carbon fibre with NTE material embedded is 775.28 MPa, which is much more than that of carbon fibre plate. From Figure 5., two curves are nearly the same at the beginning, when displacement just exceeds about 0.7mm, the curve of sample without NTE materials sheets embedded starts to slip, which means that the relative slip between the clamp and the sample occurred. By contrast, samples with NTE material embedded was held much firmly.

| Table 2. Results of the tensile test |
|-------------------------------------|
| Max Force(kN) | Tensile Strength(MPa) |
| Carbon fibre only  | 5.48 | 434.8 |
| NTE material embedded | 9.77 | 775.28 |

The tensile test validated that, the adding of NTE material do make carbon fibre plate held tighter by the clamps in cryogenic environment, for the NTE material’s volume expands at low temperatures, which compensate the space due to the contraction of carbon fibre plate with the temperature decreasing.

4. Conclusion

In this work, LaFe$_{11.5}$Si$_{1.5}$/Cu NTE materials were successfully synthesized. Their NTE properties and mechanical properties were tested and analyzed. The results show that their mechanical performance, elastic modulus and hardness, is excellent at cryogenic temperatures.
Then these NTE materials were stuck on carbon fibre plate in tensile test. The results show that the expansion of NTE materials at cryogenic environment can effectively fix the tested carbon fibre plate samples. The applications of NTE materials in tensile test and other mechanical property supply simple and useful solutions to problem brought by materials’ contraction at low temperatures.

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