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DOI: 10.1002/adem.((please add manuscript number))

Remarkable improvement of damping capacity of Mn-20Cu-5Ni-2Fe (at. %) alloy by zinc element addition**

By *Dong Li, Wenbo Liu, * Ning Li, Jiazhen Yan and Sanqiang Shi*

[*] *Prof. Dr. W. Liu, Prof. Dr. N. Li, Dr. J. Yan, D. Li*
School of Manufacturing Science and Engineering, Sichuan University, Chengdu, 610065, P. R. China
E-mail: liuwenbo_8338@163.com.
Prof. Dr. W. Liu, Prof. Dr. S. Shi
Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong
D. Li
Department of mechanical and electrical engineering, Chengdu Aeronautic Polytechnic, Chengdu, China

[**] *We give thanks to financial support by the National Natural Science Foundation of China (11076109), the Hong Kong Scholars Program (XJ2014045, G-YZ67), the China Postdoctoral Science Foundation (2015M570784), the International S&T Cooperation and Exchange Program of Sichuan Province (2017HH0068), the Scientific Research Fund of Sichuan Provincial Department of Education (16ZB0002), and the Talent Introduction Program of Sichuan University (YJ201410).*

In this paper, the effect of Zn element addition on martensitic transformation and damping capacity of Mn-20Cu-5Ni-2Fe (at.%, M2052) alloy has been investigated systematically by using X-ray diffraction, optical microscopy and dynamic mechanical analyzer. The results show that martensitic transformation and damping capacity have a crucial dependence on the addition of Zn element. It not only can markedly enhance the damping capacity of M2052 alloy at room temperature (internal friction Q^{-1} increases by ~23% compared to M2052 without Zn as strain amplitude reaches 4×10^{-4}), but also reduces the attenuation of damping capacity effectively at elevated temperatures. This is mainly because the addition of Zn element can evidently increase the Gibbs free energy difference between γ parent phase and γ′ phase produced by face centered cubic to face centered tetragonal (f.c.c-f.c.t) phase transformation, and then raises the martensitic transformation and its reverse transformation temperatures, eventually leading to the apparent increase of amount of f.c.t γ′ phase micro-

twins as damping source and the significant enhancement of damping capacity. It will be of great value for design and optimization of high-performance M2052 damping alloy towards practical applications.

1. Introduction

Manganese-copper based alloys have been widely concerned and studied because of their excellent damping capacity, mechanical property, and processability.[1] Initially, they were just used in the navigation field,[2-4] but since it was found that they possessed superior damping capacity which cannot be disturbed by magnetic field, especially at low strain amplitudes, this kind of alloy has so far been extensively applied to other industrial fields such as aerospace, automotive, and mechanical manufacturing fields.[5]

The high damping capacity of Mn-Cu based alloys can be attributed to the mobility of internal boundaries, mainly including {110} twin boundaries and phase boundaries.[6-7] The dissipation of vibrational energy by the movement of these boundaries under alternate stress makes this kind of alloy show high damping characteristics. Studies have shown that through the f.c.c-f.c.t phase transformation, the {110} twinning microstructure can readily be obtained in quenched Mn-Cu based alloys with more than 82 at.% Mn, which makes it take on good damping capacity.[8] Generally, the higher the Mn concentration in alloys is, the higher the martensitic transformation temperature (M_s) is, the more the f.c.t γ' phase micro-twins as damping source obtained at room temperature (RT) is, thus the better the damping capacity is.[9-11] However, the higher Mn concentration would directly cause the alloy brittler, and other severe problems such as the lower elongation, impact toughness and corrosion resistance. Moreover, the alloys with high Mn content are always difficult to machining, which will also go against their practical industrial applications. Therefore, in order to get both high damping capacity and good mechanical property simultaneously, Mn-Cu based alloys with Mn concentration of ~70 at.% are often used in many branches of industry, and in the meantime some alloying elements were added to further improve their overall performance. Among various Mn-Cu based alloys with relatively low Mn concentration, the M2052 alloy developed by Kawahara et al.[5] has a good sweet spot among damping capacity, yield strength and workability, indicative of tremendous potentials for practical applications in the near future. Unfortunately, the M_s of M2052 alloy is below RT,[12] and as a result, the alloy cannot be easy to get f.c.t γ' phase micro-twins by quenching. It has been reported that ageing treatment is an effective way to enhance the M_s of M2052 alloy up to above RT, which originates from the formation of nanoscale Mn enrichment by spinodal decomposition. In this case, martensitic transformation can begin at higher temperatures in the cooling process of alloy, leading to the effective formation of f.c.t γ' phase micro-twins at RT.[11,13] Even so, there are still some key problems that need to be solved further in order to gain better effect in practical applications, such as relatively low M_s, insufficient martensitic transformation, and low service temperature.

To solve these issues, researchers have so far carried out many studies on M2052, such as alloying, pre-deformation, heat treatment and molding, in which alloying is one of the most effective approaches. Recently, a kind of novel MnCuNiFeZnAl alloy with superior damping capacity and high usage temperature has been obtained through co-additions of Zn and Al elements into M2052 alloy in our previous work,[14] but unfortunately the effect of single Zn or Al element cannot be demonstrated clearly. So in this report, Zn element was individually added into M2052 quaternary alloy to clarify its influence on martensitic transformation and damping capacity, which would be critical to profound understanding of damping mechanism, as well as component design and performance optimization of Mn-Cu based high damping alloys toward engineering applications.

2. Experimental procedure

Mn-20Cu-5Ni-2Fe (at.%) and Mn-19.6Cu-4.9Ni-2Fe-2Zn (at.%) alloy ingots were prepared by a ZG-25A vacuum induction melting furnace with pure metals (electrolyzed manganese, electrolytic copper, industrial pure iron, electrolytic nickel and metal zinc) in an argon atmosphere. The alloy ingots of φ80 mm in diameter were homogenized at 850 °C for 24 hrs firstly and then forged into plates of 150 mm×15 mm in cross section. After holding at 900 °C for 1 hr, the plates were quenched in cool water, and single γ phase solid solution was obtained. Subsequently, the specimens cut from the plates were aged at 435 °C for 4 hrs, which then would be subjected to different tests. The specific chemical compositions and heat treatment conditions of specimens are shown in Table 1.

Dynamic Mechanical Analysis (DMA, Q800 TA Instruments, Inc.) was employed for damping capacity measurement of specimens. The damping capacity was characterized by Q^{-1}, which can be determined by Eq. (1) as follows:

$$Q^{-1} = Tan\delta \qquad (1)$$

where δ is the phase lag between stress and strain when the specimen is subjected to cyclic loading. So the greater the retardation angle is, the higher the damping capacity is. The damping capacity of each specimen was measured by dual-cantilever mode at a test frequency of 1 Hz, with standard dimensions of 1 mm×10 mm×35 mm. The surface strain was from 1×10^{-5} to 5×10^{-4}. The M_s is characterized by a sharp minimum in the temperature variation of storage modulus, which also was measured by DMA.

Specimens for metallographic observation, in sizes of 5 mm×5 mm×1 mm, were electrolytic polished in a mixed electrolyte of 30 ml phosphoric acid, 30 ml glycerol and 40 ml alcohol after mechanical polishing. The phase structure and lattice parameters of specimens were identified by X-ray diffraction (XRD) with Cu Kα radiation. Panalytical X'pert Pro X-ray diffractometer was operated at 40 kV and 40 mA, scanning speed: 0.06°/s. The specimens for XRD measurement, in sizes of 10 mm×10 mm×1 mm, were prepared carefully by removing surface strain.

3. Results and discussion

Fig. *1* shows the strain-amplitude dependence of Q^{-1} of M2052 alloys without and with Zn at a test frequency of 1 Hz. As can be seen clearly, both two specimens exhibit strain-amplitude-dependent damping capacity with extremely similar change tendency, which can be attributed to a static hysteresis from migration of {110} twin boundaries.[15-16] Furthermore, the damping capacity of specimen 2# was improved significantly in comparison with the M2052 alloy without Zn (specimen 1#), especially at relatively large strain amplitudes. Typically, the Q^{-1} of specimen 2# increased by ~23% relative to that of M2052 alloy without Zn as strain amplitude reaches 4×10^{-4}.

Martensitic transformation is a non-diffusion phase transformation. Usually, the soft mode mechanism is at work in metal or alloy phase transition, and as a result, the M_s of Mn-Cu based alloys could be featured by the lowest point of storage modulus softening.[17-18] Fig. *2* shows the temperature dependence of storage modulus of M2052 alloys without and with Zn. It can be seen clearly that the M_s of M2052 alloy without Zn is ~50°C, while adding Zn to the alloy increases the M_s up to ~58°C, 8°C greater than that of the M2052. Moreover, the minimum value of storage modulus of M2052 alloy with Zn is enhanced, which is closely related to the elasticity of alloy. As Zn is added to M2052 alloy, the crystal c-axis compression will increase, resulting in the improvement of elastic modulus and the enhancement of storage modulus of alloy. Also, it should be noted in Figure 2 that the reverse martensitic transformation temperature of specimen 2# increases by ~5°C compared to that of the M2052 alloy, suggesting that the damping alloy with Zn can work effectively at higher temperatures.

It has been recognized that the quick attenuation of damping capacity at elevated temperatures is a tremendous challenge for Mn-Cu based alloys.[14] Fig. *3* shows the effect of test temperature on damping capacity of M2052 alloys without and with Zn. It can be found that the damping capacity of specimen 2# are much higher than that of M2052 without Zn at 60°C and 75°C respectively, indicating that the addition of Zn element into M2052 alloy can effectively inhibit the quick attenuation of damping capacity at elevated temperatures and make it used properly at higher temperatures.

Fig. *4* shows the XRD patterns of M2052 alloys without and with Zn after the ageing. As can be seen from Fig. *4* (a), the f.c.c γ and f.c.t γ′ phases co-exist in the two specimens, corresponding to the diffraction peaks of (111), (200), (220) planes of γ parent phase and (202) plane of generated γ′ phase, respectively. When specimens were cooled to RT after the ageing, the (220) diffraction peak of γ parent phase occurred to split and generated the f.c.t γ′ phase by f.c.c-f.c.t phase transformation, which is the major source of damping capacity. Therefore, we can know that the f.c.t γ' phase is the key factor to obtain high damping capacity. Fig. *4* (b) shows the (220) peak splitting of γ parent phase in the two specimens. Clearly, both diffraction intensity and peak width of f.c.t γ' phase increase and the peak splitting is more obvious when Zn was added to M2052, implying that more damping sources can be achieved at RT for M2052 alloy with Zn.

As well-known, the atomic radii of Mn and Cu are 0.126 nm and 0.157 nm but that of Zn is 0.135 nm, so the lattice distortion (*a/c-1*) will be increased when Mn atoms are replaced by Zn in the M2052 alloy due to their closer atom radii. In this case, the *a/c-1* value can be estimated according to Eq. (2) below, as listed in detail in Table 2. According to the calculation results, we can find that as Zn is added in M2052 alloy, the c-axis of γ' phase is compressed and the a-axis is stretched, leading to the tetragonality (c/a) decrease and lattice distortion increase.

$$\frac{1}{d^2} = \frac{H^2+K^2}{a^2} + \frac{L^2}{c^2} \tag{2}$$

According to Clochard’s magneto mechanical damping model,[19] the damping capacity of alloy is proportional to the magneto elastic constant (λ) under same strain amplitudes, and the λ value can be estimated by Eq. (3):[20]

$$\lambda = \frac{1}{2} V_f \left(\frac{a-c}{c}\right) \tag{3}$$

where V_f denotes the total volume fraction of antiferromagnetic Mn-rich regions. From this, we can see that the damping capacity of alloy is proportional to the lattice distortion, and thus the larger the lattice distortion is, the better the damping capacity is. This is why the damping capacity of M2052 with Zn is far higher than the original one.

Nanoscale Mn-rich and Cu-rich regions corresponding to typical tweed structure in TEM images can be created in Mn-Cu based damping alloys by spinodal decomposition after ageing at 400～500°C for 4 hrs,[9, 21-22] which also have been confirmed by TEM observation and EDX analysis in this work (the typical sweed structure and line-scan EDX results can be seen in Fig. S1, Supporting Information). It has been reported that if the f.c.t γ′ phase can be formed at RT, the Mn concentration (C_{Mn}) in nanoscale Mn-rich regions must be more than 83.4%, and the quantitative relationship between C_{Mn} and c/a can be expressed as Eq. (4).[11, 23] According to the calculated a and c values of γ′ phase for two specimens in Table 2, the C_{Mn} in nanoscale Mn-rich regions upon spinodal decomposition can be estimated for each specimen, as present in Table 3. Evidently, the higher Mn content in nanoscale Mn-rich regions after spinodal decomposition can be obtained in specimen 2# where Zn element was added.

$$c/a = 2.638 - 3.317C_{Mn} + 1.618{C_{Mn}}^2 \qquad (4)$$

Fig. 5 shows the metallographic micrographs of M2052 alloys without and with Zn after the ageing. Clearly, a large amount of martensitic twins can be observed in the two specimens. It should be noted that, however, the width of martensitic stripe in specimen 2# just is 1~2 μm, much narrower than that in specimen 1# (3~4 μm), and the amount of martensitic stripe is also more in specimen 2#. The present results indicate that when the M2052 alloy with Zn is cooled to RT after the ageing, more and finer f.c.t γ′ phase micro-twins can be produced, thus improving the damping capacity remarkably.

From the standpoint of thermodynamics, since produced γ' phase and γ parent phase are of same compositions but different crystal structures (γ: f.c.c; γ': f.c.t), the Zn addition into

M2052 will cause the change in unit cell volume of γ phase and lead to a great elastic distortion energy, which is a strong driving force for f.c.c-f.c.t phase transformation during the cooling of alloy from 435°C to RT. According to the regular solution model,[24-25] the change of Gibbs free energy of system $\Delta G^{\gamma\rightarrow\gamma'}$ at temperature T can be evaluated by Eq. (5) as follows:

$$\Delta G^{\gamma\rightarrow\gamma'} = \Sigma X_i G_i^{\gamma\rightarrow\gamma'} + RT\Sigma X_i lnX_i + \Delta G_E^{\gamma\rightarrow\gamma'} + \Delta G_{mg}^{\gamma\rightarrow\gamma'} \tag{5}$$

where $G_i^{\gamma\rightarrow\gamma'}$ is the variation of Gibbs free energy of pure component i as martensitic transformation occurs, X_i is the mole fraction of pure component i, R is the gas constant, T is the absolute temperature, $\Delta G_E^{\gamma\rightarrow\gamma'}$ is the excess free energy, and $\Delta G_{mg}^{\gamma\rightarrow\gamma'}$ is the magnetic phase transition contribution to Gibbs free energy. It has been reported that when the C_{Mn} is over 82% in Mn-Cu based alloys, Neel temperature (T_N) will be quite higher than M_s, thus the contribution of magnetic phase transition to free energy can be negligible.[26] In this case, when Zn element is added to M2052, the absolute value of $\Delta G^{\gamma\rightarrow\gamma'}$ will be increased due to the obvious reduction of items $\Sigma X_i G_i^{\gamma\rightarrow\gamma'}$, $RT\Sigma X_i lnX_i$ and $\Delta G_E^{\gamma\rightarrow\gamma'}$, eventually resulting in the enhancement of M_s of alloy. Therefore, the γ' phase created by f.c.c-f.c.t phase transformation is more as the alloy with Zn is cooled to RT, and the damping capacity is better.

Based on our present findings, it can be proposed that the addition of Zn element into M2052 alloy can effectively raise the martensitic transformation and its reverse transformation temperatures, which will bring about two main contributions as follows. On one hand, the increase of M_s can make the alloy get more f.c.t γ' phase micro-twins as damping source when cooled to RT after the ageing, which can remarkably improve the damping capacity of alloy, especially at relatively high strain amplitudes. On the other hand, the raise of reverse martensitic transformation temperature can reduce the quick attenuation of damping capacity at elevated temperatures and makes the disappearance of annealing twins occur at higher temperatures, indicating that the service temperature of damping alloy is enhanced effectively, which is of vital importance for engineering applications.

4. Conclusions

(1) The damping property of M2052 alloy has been remarkably improved by Zn element addition, in which both martensitic transformation and damping capacity have a crucial dependence on Zn. Compare to the original M2052 alloy, the Q^{-1} increases by ~23% upon Zn addition as strain amplitude reaches 4×10^{-4}.

(2) The addition of Zn element can effectively enhance the M_s of M2052 alloy, resulting in the increase of amount of produced f.c.t γ' phase micro-twins as the alloy is cooled to RT after ageing at 435°C for 4 hrs, which can act as damping source to significantly improve the damping capacity.

(3) The addition of Zn element into M2052 also can increase the reverse martensitic transformation temperature and reduce the quick attenuation of damping capacity at elevated temperatures, leading to the obvious raise of service temperature of alloy. It will be of positive significance to design and optimization of high-performance Mn-Cu based damping alloys toward engineering applications.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

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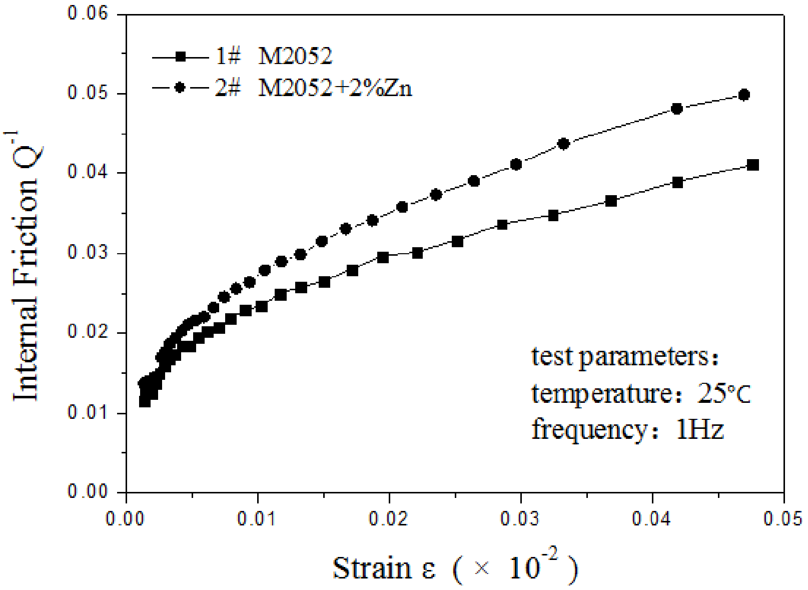

Fig. 1. Strain-amplitude dependence of Q^{-1} *of M2052 alloys without and with Zn.*

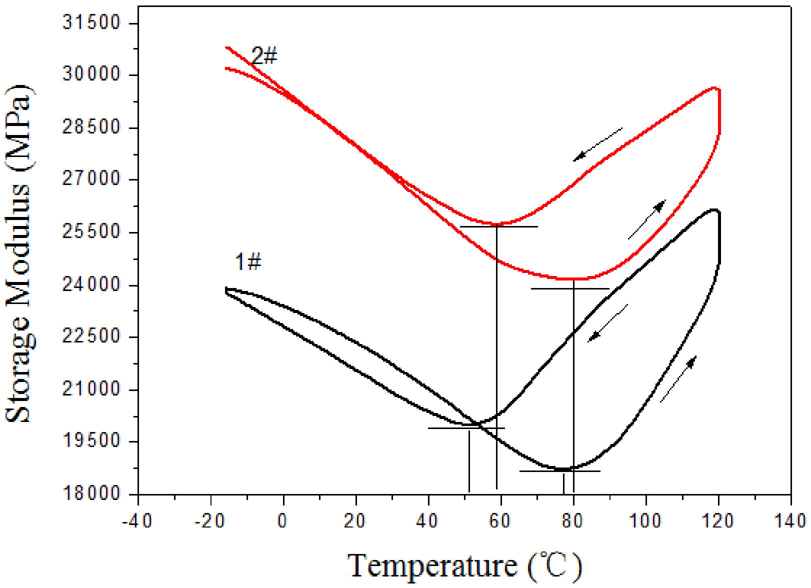

Fig. 2. Temperature dependence of storage modulus of M2052 alloys without and with Zn.

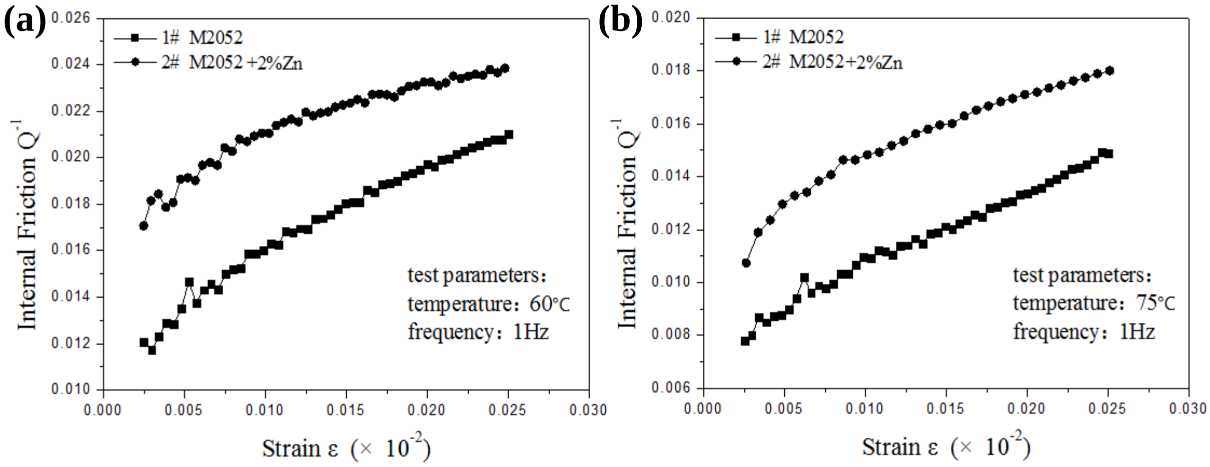

Fig. 3. Effect of test temperature on damping capacity of M2052 alloys without and with Zn. Test temperature: (a) 60°C and (b) 75°C.

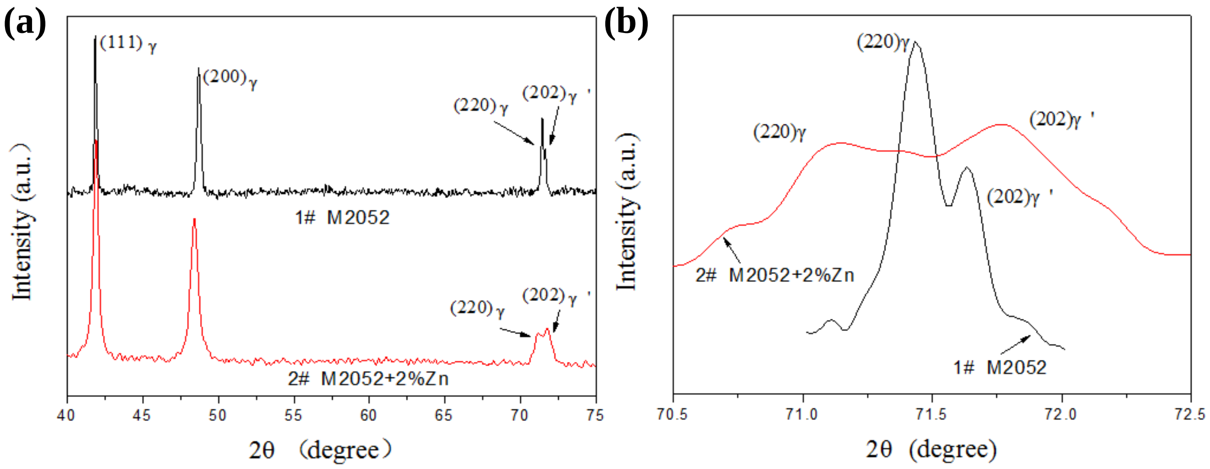

Fig. 4. (a) XRD patterns of M2052 alloys without and with Zn after the ageing; (b) Clear splits of {220} characteristic peaks at a high-magnification.

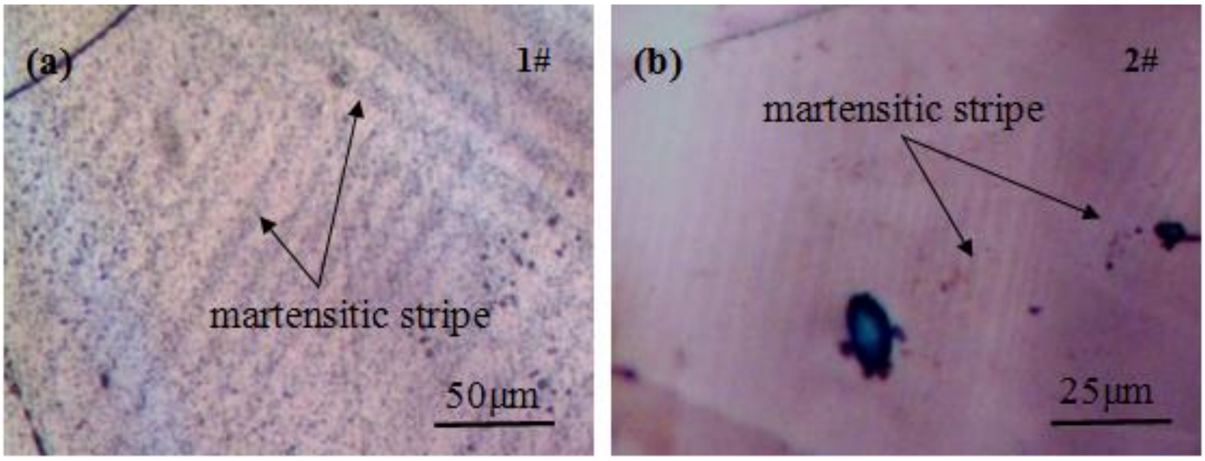

Fig. 5. Metallographic micrographs of M2052 alloys (a) without and (b) with Zn.

Table 1. Chemical compositions (at.%) and heat treatment conditions of specimens.

Specimens series	Heat treatment conditions	Mn	Cu	Ni	Fe	Zn
1#	Aged at 435°C for 4 hrs	Bal.	20	5	2	--
2#		Bal.	19.6	4.9	2	2

Table 2. Calculated lattice parameters and lattice distortions of f.c.t γ′ phase in M2052 alloys without and with Zn by Eq. (2).

	Lattice Parameter [Å]				
Specimens	Indexed interplanar spacing		Calculated lattice parameter		Lattice Distortion
	d_{220}	$d_{022\&202}$	a	c	a/c-1
1#	1.3197	1.3163	3.7327	3.7138	0.0050
2#	1.3248	1.3137	3.7465	3.6884	0.0157

Table 3. Comparison between average Mn content in alloy before spinodal decomposition and C_{Mn} in nanoscale Mn-rich regions after spinodal decomposition.

Specimens	1#	2#
Average Mn content in alloy before spinodal decomposition	73.0	71.5
C_{Mn} in nanoscale Mn-rich regions after spinodal decomposition	83.7	85.6

In this paper, the effect of Zn addition on martensitic transformation and damping capacity of M2052 alloy is investigated systematically. Results show that they have a crucial dependence on Zn addition. It not only can markedly enhance the damping capacity of M2052 alloy at room temperature (internal friction Q^{-1} increases by ~23% as $\varepsilon = 4\times10^{-4}$), but also reduces the attenuation of damping capacity effectively at elevated temperatures. This is mainly because the Zn addition can raises the martensitic transformation temperature (M_s) from 50°C up to 58°C, thus leading to the apparent increase of amount of f.c.t γ' phase micro-twins as damping source.

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ToC figure ((48 mm broad))