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Journal of Magnesium and Alloys 12 (2024) 659-672

www.elsevier.com/locate/ima

Full Length Article

Wettability, reactivity, and interface structure in Mg/Ni system

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Received 28 August 2023; received in revised form 10 November 2023; accepted 2 January 2024 Available online 16 January 2024

Abstract

The sessile drop method was applied to the experimental investigation of the wetting and spreading behaviors of liquid Mg drops on pure Ni substrates. For comparison, the experiments were performed in two variants: (1) using the Capillary Purification (CP) procedure, which allows the non-contact heating and squeezing of a pure oxide-free Mg drop; (2) by classical Contact Heating (CH) procedure. The high-temperature tests were performed under isothermal conditions (CP: 760 °C for 30 s; CH: 715 °C for 300 s) using Ar + 5 wt% H₂ atmosphere. During the sessile drop tests, images of the Mg/Ni couples were recorded by CCD cameras (57 fps), which were then applied to calculate the contact angles of metal/substrate couples. Scanning and transmission electron microscopy analyses, both coupled with energy-dispersive X-ray spectroscopy, were used for detailed structural characterization of the solidified couples.

It was found that an oxide-free Mg drop obtained by the CP procedure showed a wetting phenomenon on the Ni substrate (an average contact angle $\theta < 90^{\circ}$ in < 1 s), followed by fast spreading and good wetting over the Ni substrate ($\theta_{(CP)} \sim 20^{\circ}$ in 5 s) to form a final contact angle of $\theta_{f(CP)} \sim 18^{\circ}$. In contrast, a different wetting behavior was observed for the CH procedure, where the unavoidable primary oxide film on the Mg surface blocked the spreading of liquid Mg showing apparently non-wetting behavior after 300 s contact at the test temperature.

However, in both cases, the deep craters formed in the Ni substrates under the Mg drops and significant change in the structure of initially pure Mg drops to Mg-Ni alloys suggest a strong dissolution of Ni in liquid Mg and apparent values of the final contact angles measured for the Mg/Ni system.

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Keywords: Magnesium-based alloys; Sessile drop tests; Capillary purification procedure; Wettability; Reactivity; Contact angle.

1. Introduction

Understanding the high-temperature wetting behavior in liquid metal/solid substrate systems is of practical interest to improve industrial processes and the quality of the products obtained, especially when supported by the liquid phase. Therefore, knowledge of the high-temperature interactions of liquid metals with dissimilar solid materials is one of the most important scientific aspects required in modern metallurgy and foundry engineering [1]. Methodological discrepancies and inconsistencies in the characterization of liquid metal/substrate wettability between different laboratories and research groups are the main sources of disagreement in the measurements of thermophysical properties, i.e. surface tension of molten metals and alloys, contact angle or work of adhesion between dissimilar materials. The high sensitivity of these parameters to test conditions leads to significant differences between test data for a given system obtained by various researchers [1-4].

In addition, the wrong choice of container during the preparation of alloys and new metal matrix composite materials by liquid-assisted techniques can result in their contamination during manufacturing. Consequently, it can cause structural defects in final products (cracks, inhomogeneity, segregation, porosity, etc.), while their properties become unsatisfactory and the tests performed on them give unreliable results and lead to erroneous conclusions. Therefore, reliable data on thermophysical properties should allow optimization

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https://doi.org/10.1016/j.jma.2024.01.008

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of the selection of refractory materials used in casting processes (e.g., crucibles or molds) [1,2,5–7]. In addition, today's advanced materials engineering is based on computer simulations and predictions, and reliable simulations can be made only when accurate thermophysical data are available [1].

Magnesium and its alloys have a wide range of applications in various industries and daily life [8]. They are lightweight and strong materials with better ductility and castability than aluminum and steel [8,9]. The current trend is to replace structural materials, i.e. steel, with strong materials in hybrid structures. Steel and magnesium are known to be immiscible and unreactive, even in the liquid state, making it challenging to combine these two materials [10]. Consequently, their industrial applications are limited. To join such dissimilar materials as Mg to steel or Ti, it is necessary to use technologies coatings, which play the role of intermediate layers, that are wetted by liquid Mg [10–14]. According to the literature, the addition of an interlayer, such as Ni [10,13,14], increases the wettability and allows the permanent bonding of Mg to materials that normally cannot be joined by liquidassisted techniques without an interlayer because they do not exhibit wetting behavior with liquid Mg, such as steel.

It should be highlighted that there is limited available information about the high-temperature interaction between Mg and dissimilar materials with only a few papers. The first pioneering study was reported by Kondoh et al. [15], who performed a systematic analysis of factors affecting the wetting and spreading behaviors of liquid Mg on pure Ti and TiO₂-coated Ti substrates at 800 °C using the classical contact heating procedure of the sessile drop method. Despite the obtained unique experimental data, the temperature used by Kondoh et al. [15] was too high and far from those of practical importance, while their results were strongly affected by the evaporation of Mg that takes place at such high temperatures.

Therefore, the main objective of this work is to determine, for the first time, the high-temperature behavior of liquid magnesium in contact with a pure nickel substrate by the sessile drop method at temperatures of 760 °C and 715 °C, using two different testing procedures: (1) capillary purification coupled with non-contact heating and (2) classical contact heating to the test temperature, respectively. The results obtained enrich the limited information available on the high-temperature interactions of liquid Mg with various materials [8,9,16]. Furthermore, Ni is one of the most widely used alloying additives for steel to increase its corrosion resistance. Furthermore, investigating the interaction between molten Mg and solid Ni is of practical importance for the determination of whether nickel-based or nickel-rich alloys, i.e., stainless steel or Inconel, can be used as materials for casting and fabrication of Mg alloys.

2. Experimental procedures

2.1. Wettability tests

The study of wetting and reactivity phenomena between liquid magnesium (\geq 99.99 wt%) and solid nickel substrate

(99.9 wt%) was performed by the sessile drop method using a unique apparatus, described in detail in a previous paper [9]. Two testing procedures were applied in this study for real-time observation of melting Mg, its wetting and spreading behaviors over Ni substrate at the test temperature, and final solidification of Mg/Ni couples produced in the sessile drop tests: Capillary Purification (CP) and classical Contact Heating (CH). The advantage of the CP procedure over the CH procedure is that it allows non-contact heating of the liquid drop material and substrates to the experimental temperature, thus avoiding the heating history of the Mg/Ni couple. In addition, by squeezing the liquid metal out of a graphite capillary placed above the substrate, the CP procedure makes possible mechanical cleaning of the Mg drops from the native oxide film directly in the experimental chamber [5,9,16,17].

A magnesium rod (\geq 99.99 wt%) with a diameter of 11 mm and a height of 14 mm was used for the CP procedure, the surface of which was polished with sandpaper before the measurements and then cleaned in pure isopropanol for about 15 min in an ultrasonic bath. Then, the cleaned rod was immediately inserted into a graphite capillary that was placed in the vacuum chamber and the device was pumped down. In the case of the CH test, an irregular piece of Mg rod with the dimensions shown in Fig. 1c was taken from the same material used for the CP measurement. The surface of such an Mg half rod was then cleaned analogously to the Mg used in the CP procedure. The final material was carefully placed in the center of the polished Ni substrate, as shown in Fig. 1c, and inserted into the cold measurement furnace. The shape of the Mg sample, as well as its positioning, was deliberately chosen so that the melting moment of the sample could be clearly observed.

It should be highlighted that the Ni substrates used in this study had dissimilar surface finish, i.e. in the CP test (Fig. 1a), it was not subjected to polishing before the measurement. However, it was cleaned for around 15 min in an ultrasonic bath containing pure isopropyl alcohol. In contrast, in the test performed using the CH procedure, the surface of the Ni substrate was polished with sandpaper (gradation 220–7000) and with diamond pastes (3–1/4 μ m) and nano-SiO₂ suspension according to the procedure specifications [7]. The Ni substrate prepared in this way (Fig. 1b) was washed in pure isopropanol for about 20 min in an ultrasonic cleaner.

Then, after the Mg sample and Ni substrate were placed in the measurement chamber (regardless of the procedure used), the device was pumped to a pressure of 10^{-6} mbar. Next, a flowing inert gas (a mixture of Ar + 5 wt% H₂) was introduced into the chamber, and when the gas pressure reached 1.10×10^3 mbar, the chamber was pumped again to a vacuum of 10^{-6} . This operation was performed to clean the chamber. After the high vacuum was reached, the Ni substrate and Mg sample were isothermally heated to about 400 °C to remove, among other things, residual water vapor and other volatile substances from the Ni and Mg surfaces. Finally, a gas mixture of Ar + 5 wt% H₂ was again introduced into the test chamber (up to 1.10×10^3 mbar) and heating was continued to the desired test temperature.



Fig. 1. Top-view photos of the nickel substrate before (a), (b), (c), and after the sessile drop experiments (d) using CP procedure: 760 °C/Ar + 5 wt% H₂, and (e) using CH procedure: 715 °C/ Ar + 5 wt% H₂.

In the case of the sessile drop test with the CP procedure, the Mg drop was deposited on the Ni substrate at a temperature of $T_{exp(CP)}$ = 760 °C and next, the Mg/Ni couple was isotermally heated for 30 s only. For the CH test, the applied temperature was lower, i.e. $T_{exp(CH)} = 715$ °C, and after reaching this temperature, the Mg/Ni couple was held for a time of 300 s. It should be highlighted that from our previous experience with testing liquid Mg, its test temperature should not be increased above 715 °C when longer contact time is needed (e.g. in our CH test) because of the very evaporation of Mg that may affect the substrate surface chemistry and may cause contamination or even damage of equipment components. For both CP and CH tests, the heating rate was 10 °C/min and they were performed in the presence of Ti (99.99 wt%) chips and sponge, which were placed next to the Ni substrate to function as oxygen absorbers [1,9]. Moreover, immediately after the test but still at the measurement temperature, both the CP and CH Mg/Ni couples were quickly removed from the furnace chamber into the delivery chamber located next to the furnace [9], where the temperature is close to room temperature, thus somehow freezing the structure of the Mg/Ni couples. Fig. 1d and e show the Mg/Ni couples after high-temperature tests. During the test, continuous imaging of Mg/Ni couples was recorded using high-speed and high-resolution digital CCD cameras with a rate of 57 frames per second. The collected images were undergo computer image analysis using specialized DROP software [18].

This software was used to calculate the contact angle (θ) and wettability kinetics $\theta = f(t)$ of the investigated system.

2.2. Microstructure observations

2.2.1. Scanning electron microscopy observations

Detailed microstructural studies were carried out on solidified Mg/Ni couples after the high-temperature tests. An FEI E-SEM XL30 scanning electron microscope (SEM) was used for this purpose. This microscope is equipped with an EDAX GEMINI 4000 energy dispersive X-ray spectrometer (EDS) for chemical composition analysis. A top view of the couples was taken first, followed by a cross-sectional examination. For the latter, metallographic specimens were prepared by embedding the sessile drop Mg/Ni couples in epoxy resin, cutting them, then polishing with the use of sandpapers (gradation from 220 to 7000) and anhydrous diamond pastes $(3-1/4 \ \mu m)$ and finishing with a nano-SiO₂ suspension to obtain a mirror-like surface. A thin layer of amorphous carbon was deposited on the metallographic samples to ensure good electrical conductivity during SEM studies and to prevent oxidation [9,17]. All microstructure observations and chemical composition analyses were conducted with an accelerating voltage of 15 kV with a spot size of 5.0 and a working distance of 10 µm. The images were recorded at magnifications from 50 \times to 5 000 \times . The observations were made using a backscattered electron (BSE) detector.



Fig. 2. Images recorded by the CCD camera during the sessile drop tests of Mg/Ni couple under flowing mixture of gases Ar + 5 wt% H₂:(a) using CP procedure, (b) using CH procedure; the last image for both sets corresponds to the end of the test after isothermal contact for (a) 30 s and (b) 300 s.

2.2.2. Transmission electron microscopy observations

More detailed microstructure investigations, as well as phase and chemical analysis, were performed with FEI Tecnai G2 200 kV transmission electron microscope equipped with SIS MegaView III CCD camera for recording microstructure photographs diffraction patterns. The chemical composition was determined with EDAX energy dispersive X-ray spectrometer (EDS). The phase analysis was done through indexing of selected area electron diffraction (SAED) patterns with Carine computer software. The TEM analysis was done on the thin foils having ~100 nm in thickness to secure the transparency for the electron beam. They were prepared from the bulk samples with the use of the focused ion beam (FIB) technique (Ga⁺ ion beam) and a ThermoFisher Scios 2 Dual Beam microscope equipped with an EasyLift nanomanipulator.

3. Results and discussion

A selection of images of the liquid Mg/Ni couples can be seen in Fig. 2. They were captured by the high-speed digital CCD camera at 57 frames per second. The images in Fig. 2a show the characteristic steps of the sessile drop test using the CP procedure (drop squeezing, drop deposition, the release of the graphite capillary from the drop, drop dissolution and spreading, end of test) taken while held at $T_{exp(CP)}$ in an atmosphere of Ar + 5 wt% H₂ mixture for 30 s. Meanwhile, Fig. 2b illustrates the stages of the classical contact heating procedure test (before heating, during heating and reaching magnesium melting point, end of test), recorded during heating to $T_{exp(CH)}$, where the Mg/Ni couple was held for about 300 s.

The changes in the values of the left contact angle (θ_1) , the right contact angle (θ_r) , and their average values (θ_{av}) as a function of time, i.e. the wetting kinetics curves for hightemperature measurements for Mg/Ni couples, are shown in Fig. 3.

Fig. 3a shows the wetting kinetics results recorded during a 30 s measurement using the advanced CP procedure, while Fig. 3b represents the wetting kinetics curve for the couple obtained during the test with the use of the conventional CH procedure. The values of contact angles were calculated at



Fig. 3. Wetting kinetics of liquid Mg on the Ni substrates registered during the sessile drop test by (a) the CP procedure (760 °C/Ar + 5 wt% H₂) for the 30 s with 0.5 s interval, (b) the CH procedure (715 °C/Ar + 5 wt% H₂) for 300 s with 5 s interval, (c,d) QR codes for real-time video of the wettability test, (c) for CP procedure, (d) for CH procedure, respectively.

0.5 s intervals for the CP test, whereas for the CH procedure, the estimated contact angle values were determined at 5 s intervals. In addition, real-time videos of sessile drop tests of Mg/Ni couples using the CP and CH procedures can be watched by scanning the QR codes shown in Fig. 3c and d, respectively.

By analyzing Figs. 2 and 3, it can be observed that the first average contact angle formed immediately after the drop is deposited on the substrate (t = 0 s) is equal to $\theta_{0(CP)} = 152^{\circ}$ (Fig. 3a). However, due to the continuous and rapid spreading of the liquid Mg over the substrate, its value steadily and rapidly decreased in about 5 s when the contact angle reached an average value of $\theta_{av(CP)} \sim 21^{\circ}$. Further holding the Mg/Ni couple at $T_{exp(CP)}$ did not cause any additional significant changes in the value of the contact angle, and finally, the average value of the contact angle stabilized at $\theta_{f(CP)} \sim$ 18°. The wetting kinetics curve indicates that under the CP testing conditions, nickel shows a good wetting by liquid Mg ($\theta << 90^{\circ}$).

In the CH test, the melting of the irregular Mg piece placed on the Ni substrate (Fig. 1c) became visible in the contacting area at $T \sim 667$ °C (Fig. 2b). When the couple is further heated, and the measurement temperature is raised, the thick oxide film surrounding the Mg sample breaks and liquid pure magnesium can be seen underneath. In this measurement, heating the sample from room temperature (RT) to the measurement temperature makes the Mg piece act as a getter, absorbing residual oxygen from the measurement chamber. Thus, secondary oxidation of the primary oxide film exists on the surface of the Mg piece, which grows and increases its thickness. The thermal expansion of MgO oxide is less than twice that of pure Mg, especially at the temperature at which Mg transforms from a solid to a liquid state [19,20]. Furthermore, the volume of Mg quickly increases during melting. As a result, the oxide film surrounding the Mg sample cracks and loses its continuity while the separated oxide pieces are scattered from the original surface. Under such circumstances, a true contact between the liquid Mg and the Ni substrate can be established is clearly demonstrated in the side-view images of the CH couple (Fig. 2) and the real-time video (Fig. 3d).

Moreover, the oxide film that still covers the CH drop surface avoids the formation of a symmetrical drop shape, acts



Fig. 4. SEM images of the cross-sectioned Mg/Ni couple obtained by the sessile drop method using the CP procedure (760 °C; 30 s), taken with the BSE detector at different magnifications: (a) general view (100 \times); (b,c) left and right edges; (d) interface in the central part of the drop; (e) the top surface of the drop; (b)–(e) magnification (1000 \times); (c) inserted image shows the magnified fragment of the corner of (c) under a 5000 \times magnification.

as a barrier for a free spreading of molten Mg and it also prevents from freely interaction with the Ni substrate. Thus, these factors affect the wetting and spreading behaviors of the drop [1,5,7,9]. Applying the CH procedure makes it difficult not only to properly measure wetting characteristics but also to correctly interpret wetting kinetics. Through this, it should be emphasized that the contact angle values shown in Fig. 3b cannot be considered as true contact angles, but only as an attempt to determine the relationship between the liquid Mg and the Ni substrate under this specific measurement conditions, when the surface of Mg is oxidized. Therefore, the measured angles indicate the non-wetting behavior of such a couple. On the other hand, because of the nature of the contactless heating process and the mechanical removal of the oxide film, the CP test produces an oxide-free Mg drop allowing its fast wetting and spreading accompanied with the rapid dissolution of the Ni substrate. These phenomena cause the drop to reach a saturated state very quickly due to the very large contact area and the fast mass transfer across the interface.

Considering the findings presented above, the significant difference in wetting behavior for the same couple of materials using different test procedures is mainly due to the presence of a primary thick oxide film on the surface of the used Mg piece when the CH procedure was applied. Such an oxide film is well-distinguished on the drop surface due to difference in brightness, i.e. matte oxidized surface vs bright oxide-free surface, as shown in Figs. 1e and 2b. Contrary to this, in the CP procedure, the molten metal squeezed from the hole in a graphite capillary is free from the native oxide film. Consequently, it allows for rapid and direct contact between the liquid metal and the substrate, and thus its reaction and dissolution, as proven by the contact angle values far below $\theta << 90^{\circ}$ [1,4,9].

The slight fluctuations in the contact angle values seen in Fig. 3 can be caused by oscillation and movement of the Mg drops due to the intense evaporation of Mg (see real-time video) [17].

Similar results on the high-temperature interaction between liquid Mg and Ni substrate using the same measurement method and CH procedure were reported by Kudyba et al. [7] for the measurements performed at 700 °C and t = 300 s in Ar (99.999 wt%) flowing gas. Table 1 presents the comparison between the results obtained in this study and those in Ref. [7].

In contrast to the results presented in this work obtained using the CH procedure, in the study of [7] the liquid magnesium spread over the surface of the Ni substrate after melting and the final contact angle was almost the same as that obtained in this work using the CP procedure for the same



Fig. 5. SEM images of the cross-sectioned Mg/Ni couple obtained by the sessile drop method using the CH procedure (715 °C, 300 s), taken with the BSE detector at different magnifications: (a) general view (50 \times); (b,c) left and right edges; (d) interface in the central part of the drop; (e) central part of the drop; (f) the top surface of the drop; (b)–(f) magnification 500 \times .

couple of materials. However, it should be emphasized that in the test performed by Kudyba et al. [7], the Mg sample on the Ni substrate was introduced directly into the hot furnace at the experimental temperature and in an atmosphere of pure argon; then, after a certain period of time, the test couple was immediately removed to the cold part of the test chamber after the wettability tests, which is crucial here. Thus, the Mg sample introduced in this way reached its melting point in a very short time, and the primary Mg oxide film quickly lost its continuity and cracked due to the volume expansion of the Mg sample during its transition from the solid to the liquid state. Next, the formed liquid could have leaked through the discontinuities in the primary oxide film, locally pushed the oxide fragments from the drop surface, near the triple point where the oxide-free liquid Mg drop was able to have a true contact with the Ni substrate, and finally to wet, spread, and react with it. In this way, the authors [7] avoided in their CH test the effect of secondary oxidation of the Mg sample covered with primary oxide film. Comparable observations of self-cleaning of the drop surface in high-temperature tests

Procedure	$T_{\rm exp}$ [°C]	Atmosphere	Time at T _{exp} [s]	Heating rate [°/min]	Cooling rate [°/min]	θ [°]	Remarks	Ref.
СР	760	Ar + 5 % H ₂	30	-	200	11	Unpolished Ni substrate. Separate heating to T_{exp} ; Mg drop deposited at T_{exp}	This study
СН	715	$Ar + 5 \% H_2$	300	10	140	132* 26**	Polished Ni substrate. Contact heating from RT with a rate of 10 °C/min	
СН	700	Pure Ar (99.999 wt%)	300	~28	-	18	Polished Ni substrate. The couple was introduced into the furnace already preheated to T_{exp}	[7]

Comparison of the sessile drop tests for Mg/Ni couples measured in this study and in Ref. [7].

* This value should not be taken as the true contact angle because of the lack of formation of a symmetrical liquid Mg drop due to its oxidation. ** The average value of contact angle estimated from the SEM image (Fig. 6) for the interaction between oxide-free liquid Mg drop and oxide-free pure Ni substrate.



Fig. 6. (a) SEM image for the area seen in Fig. 5b. at a magnification of 1000 ×; (b-c) maps of the distribution of the elements: (b) Mg and (c) Ni.

using the CH procedure have been reported in the literature for metals such as Sn, Cu, or Al and their alloys [1,21]. In the CH test of the present study, the Mg sample on the Ni substrate was heated to the tested temperature from room temperature, first in a high vacuum, and then in an atmosphere of a gas mixture of Ar + 5 wt% H₂. Such a procedure significantly affected the thickness of the oxide film on the Mg drop, which prevented both the spreading of liquid Mg on the substrate and the formation of a symmetrical liquid drop. All these observations prove that methodological aspects, especially differences in testing procedures and conditions, are crucial in the measurements of the wetting properties of Mg in contact with different metallic substrates.

Figs. 4 and 5 show representative results of the microstructural analysis of the cross-sectioned Mg/Ni couples obtained by the sessile drop method with two different test procedures, CP and CH, respectively.

SEM observations of the Mg/Ni couple obtained by the CP procedure, shown in Fig. 4, confirmed a very good wet-

ting and spreading of the molten Mg drops on the nickel substrate at 760 °C, due to the very strong chemical interaction between them [17,22,23]. Although the test was very short (~30 s), a crater (~100 μ m), characteristic of reactive systems [17,22,23], formed in the substrate under the drop, resulting from the dissolution of nickel in liquid magnesium. The formation of such a crater may suggest that the contact angles calculated from the side-view images of the drop are apparent [9,22].

In addition, the initially pure Mg drop has a multiphase composition after the CP test with the Ni substrate and subsequent solidification. The structure seen in Fig. 4 consists of a continuous light gray layer of a new phase formed at the interface between the drop and the Ni substrate, extending from the left to the right edge of the drop. This phase releases a large number of gray and long primary crystals with a well-developed surface, surrounded by a component with a characteristic eutectic structure. In addition, it can be observed (Fig. 4a) that the crystals of the new phase show directional

Table 1

Table 3 Results of EDS analysis of CP couple for phases marked in Fig. 4b-e. Results of EDS analysis of CH couple for phases marked in Fig. 5b-f.

Figure no.	Point no.	Composition points	in marked	Phases	
		Mg [at.%]	Ni [at.%]		
4b	1	29.0	71.0	MgNi ₂	
	2	27.0	73.0	MgNi ₂	
4c	3	19.9	80.1	MgNi ₂	
	4	38.3	61.7	MgNi ₂	
4d	5	77.9	22.1	$(Mg + Mg_2Ni)_{eut}$	
	6	30.4	69.6	MgNi ₂	
4e	7	39.8	60.2	MgNi ₂	
	8	78.6	21.4	$(Mg + Mg_2Ni)_{eut}$	

Table 2

solidification perpendicular to the substrate surface, i.e. in the direction of the heat flow [24]. A detailed SEM/EDS analysis of a CP couple showed that the continuous light gray phase consists of 38 at.% Mg and 62 at.% Ni, the light crystals have an average of 29 at.% Mg and 71 at.% Ni, while the Ni and Mg contents in the dark gray phase with a eutectic structure are 78 at.% and 22 at.% (Fig. 4b-e points 1-8, Table 2). As can be seen, the solidified Mg drop contains a large amount of Ni coming from the substrate, which clearly indicates the dissolution of the Ni substrate in the Mg drop.

The microstructure of the Mg/Ni couple obtained by the CH procedure is different from that of the CP couple made by the CP procedure. In this couple, a crater is also visible in the substrate under the drop, which is characteristic for reactive systems, but in this case, the crater is about four times larger ($\sim 400 \ \mu m$) than in the CP couple. Most likely, such a large crater was formed because the primary oxide film covering the surface of the Mg sample blocked the ability of the liquid Mg to spread over the Ni substrate. Thus, the dissolution of nickel in the liquid magnesium according to the dissolve mechanism and the reaction between the components could only take place deep in the substrate. Again, it can be assumed that the actual and final contact angles calculated from the side-view images of the drop taken during the sessile drop test are apparent. However contrary to the CP procedure, these CH values are overestimated because of the presence of surface oxide film on the Mg drop.

As for the results of the microstructural analysis of the CH couple, three zones appearing on the solidified side of the drop can be distinguished, where the gradient of the Ni distribution is clearly visible. The first is located at the interface between the drop and the substrate and consists of light gray crystals of different sizes. Between the crystals, a second constituent with a eutectic structure is observed, which continues homogeneously up to about one-third of the height of the Mg sample. The final region, extending to the top of the drop, consists of a dark gray phase surrounded by remnants of the eutectic mixture from the second region. In addition, a break/discontinuity between the substrate and the drop is very clearly seen running along the interface of the entire Mg/Ni couple from left to right of the drop edge. This discontinuity is probably due to Mg-Ni drop solidification. The results of

Figure no. Point no. Composition in marked Phases points Mg [at.%] Ni [at.%] 5b 1 64.6 35.4 Mg₂Ni 2 85.5 14.5 $(Mg + Mg_2Ni)_{eut}$ 3 64.7 35.3 Mg₂Ni 5c 4 64.4 35.6 Mg₂Ni 5 86.4 13.6 (Mg + Mg2Ni)eut 5d 6 85.6 14.5 $(Mg + Mg_2Ni)_{eut}$ 7 64.2 35.7 Mg₂Ni 8 5e 100.0 0 Mg

13.5

21.0

0

Table 4					
Results of EDS	analysis of	area	presented	in Fig.	6.

86.5

100.0

79.0

9

10

11

Point no.	Composition in	Phases	
	Mg [at.%]	Ni [at.%]	
1	63.9	36.1	Mg ₂ Ni
2	64.7	35.3	Mg ₂ Ni
3	64.5	35.5	Mg ₂ Ni
4	83.8	16.2	$(Mg + Mg_2Ni)_{eut}$
5	85.3	14.7	$(Mg + Mg_2Ni)_{eut}$

local SEM/EDS chemical composition analyses at the locations shown in Fig. 5b-f and listed in Table 3 indicate that the light gray crystals contain 65 at.% Mg and 35 at.% Ni, the eutectic mixture has 85 at.% Mg and 15 at.% Ni, while the dark gray phase extending to the top of the drop contains 100 at.% Mg.

As compared to the CP couple (Fig. 4a), a much smaller contact area between the molten Mg and the Ni substrate can be seen in Fig. 5b. The enlarged part of the Mg/Ni interface in the vicinity of the triple point of the Mg drop in Fig. 6 shows the small drop on the left side of the main Mg drop. Obviously, this "daughter" droplet was formed during the wettability test. Most likely it came out from under the oxide film of the main Mg drop and it is oxide-free, similar to the CP process. Thus we may conclude that in this case, the interaction of the Mg droplet with the Ni substrate corresponds to the situation of oxide-free liquid Mg on oxidefree Ni. Structural and phase analysis of the interface formed with small Mg droplet showed that the light gray crystallites emerging from the Ni substrate have a similar composition to the crystals from the crater in the CH couple (Table 4), and above them is a region with a typical eutectic structure. A small crater resulting from the high reactivity between the components is also observed here. The manually determined contact angles from the SEM image (i.e. for already solidified droplet after testing at $T_{exp(CH)} = 715$ °C) show the average value of $\theta \sim 29^{\circ}$. This value is significantly smaller than that for the CH couple (i.e. for the case of oxidized drop on the oxide-free substrate) and slightly larger than for the CP couple obtained at a higher temperature of $T_{exp(CP)} = 760 \text{ }^{\circ}\text{C}$

5f

(Mg + Mg₂Ni)_{eut}

 $(Mg + Mg_2Ni)_{eut}$

Mg



Fig. 7. Phase diagram of the Mg-Ni system [25]; the insert in (a) corresponds to the magnified region shown in (b).

(i.e. for the case of *oxide-free drop on the oxidized substrate*). These findings suggest that the possible shrinkage of the Mg-Ni droplet upon its solidification has a negligible effect on the contact angle value.

It should be emphasized that the SEM observations made on the Mg/Ni couples obtained in the high-temperature sessile drop tests performed by two different procedures were carried out on solidified drops, the structure of which is strongly dependent on the heating, cooling, and solidification history (in the case of the CP procedure, only the last two parameters are decisive [9]). Therefore, in order to clarify the main steps of the high-temperature interaction between the liquid Mg drop and the Ni substrate during the wettability test, the detailed SEM/EDS characterization of the cross-sectioned Mg/Ni couple (Table 2) was supported by the analysis of the Mg-Ni phase diagram (Fig. 7) obtained using the FactSage software



Fig. 8. TEM/BF images and corresponding SAED patterns acquired from the cross-sectioned Mg/Ni couple obtained by the sessile drop method using the CP procedure: (a) interface between Ni substrate and solidified Mg drop with (b) maps of elements distribution and (c) eutectic mixture with (d) maps of elements distribution.







Fig. 9. TEM/BF images and corresponding SAED patterns acquired from the cross-sectioned Mg/Ni couple obtained by the sessile drop method using the CH procedure: (a) $Mg + Mg_2Ni$ eutectic mixture adjacent to Mg_2Ni crystal (close to the substrate material) with (b) maps of elements distribution and (c) $Mg + Mg_2Ni$ eutectic mixture adjacent to pure magnesium (farther from the substrate material) with (d) maps of elements distribution.

and the FTlite database [25]. Because the two sessile drop Mg/Ni couples were obtained at dissimilar temperatures and using different test procedures, the interpretation of the results using the phase diagram is different for each of the drop/substrate couples.

From the EDS results and the Mg-Ni phase diagram (Fig. 7), it can be concluded that in the case of the Mg/Ni couple obtained at a higher temperature of 760 °C by the CP procedure, the composition of the continuous light gray and light long crystals on the substrate side corresponds to the MgNi₂ phase, while the dark gray region is eutectic $(Mg + Mg_2Ni)_{eut}$.

In contrast, for the Mg/Ni couple obtained at a lower temperature of 715 °C by the CH procedure, it can be assumed that the chemical composition of the light crystals (Fig. 5b–d, points 1,3–4,7 and Fig. 6 points 1–3) corresponds to the Mg₂Ni phase that may have formed on the drop side at the measurement temperature. The second constituent (Fig. 5b–f, points 2,5–6,9,11 and Fig. 6 points 4–5) surrounding the large crystals can be identified as (Mg + Mg₂Ni)_{eut}, which surrounds the remaining pure magnesium at the top of the drop (Fig. 5f).

In both cases, according to the Mg-Ni phase diagram (Fig. 7), reactive wetting between liquid Mg and Ni substrate is possible by two mechanisms, i.e., dissolutive wetting and formation of wettable interfacial reaction products. Furthermore, it is believed that in both cases, the first contact angle measured at t = 0 s, which is $\theta_{0(CP)} = 152^{\circ}$ and $\theta_{0(CH)} = 160^{\circ}$, respectively, corresponds to the contact angle formed by pure Mg on the Ni substrate. This is followed by the dissolution of Ni in liquid Mg, as at the test temperatures (715 °C and 760 °C), liquid Mg can dissolve approximately 20 at.% and 30 at.% of Ni, respectively, resulting in a decrease in the contact angle. During sessile drop tests by both testing procedures at two dissimilar temperatures, initially, pure Mg drop is alloyed with Ni resulting in the conversion of the Mg/Ni couple to a new one (Mg-Ni)alloy/Ni. In the final step in the interaction between the Ni substrate and the liquid Mg drops saturated with Ni after isothermal heating at the test temperature is the formation or growth of a continuous MgNi₂ phase layer for the CP procedure and a Mg₂Ni phase for the CH procedure at the Mg/Ni interface.

Because in both tests, the couples were quickly removed from the test furnace, non-equilibrium solidification occurred. The cooling rate for the CP couple was ~ 200 °C/min and for the CH couple about 140 °C/min. As a result, the solubility of Ni in liquid magnesium rapidly decreases, the structure inside the drops freezes, and a hypereutectic alloy is formed. Therefore, the contents of the individual components (Tables 2–4) in the phases visible in Figs. 4–6 are higher than indicated by the Mg-Ni phase equilibrium diagram (Fig. 7).

Moreover, careful observation of the structure of the bright crystals in Figs. 4 and 5 shows that the intermetallic phases formed at the interface, although seem to be similar at first view, have different morphologies. The nickel-rich MgNi₂ phase in the CP couple (Fig. 4) is definitely more rounded and not as angular, sharp, and needle-like as the magnesium-

rich Mg₂Ni phase. Furthermore, numerous cracks and gouges can be seen in the structure of the MgNi₂ phase, indicating that a partial peritectic reaction (L + MgNi₂ \rightarrow Mg₂Ni) probably takes place during cooling in a very short time (the CP measurement was performed practically at the temperature of this transformation). This results in the partial disappearance of the MgNi₂ phase and makes the MgNi₂ crystals more rounded, chipped, and fractured.

The analysis of the SEM/EDS results and the Mg-Ni phase diagram (Fig. 7) were also supported by transmission microscopy observations. The FIB sample cut out from the cross-sectioned CP couple in the area close to the substrate showed a wavy interface between pure Ni material and solidified Mg droplet (Fig. 8a). Farther fragments of the reacted Mg drop are separated from the substrate by the thin layer (< 1 µm in thickness) of Ni-rich intermetallic phase. Indexing of the SAED patterns allowed to confirm it to be the MgNi₂ phase. The neighboring area, seen in the TEM/BF mode in the form of uniform contrast (with the occasional presence of bending contours), was proven to be the Mg₂Ni intermetallics. The TEM/BF imaging has also been performed in the area of the eutectic mixture and its constituents were confirmed by SAED as Mg + Mg₂Ni (Fig. 8c). In turn, Fig. 9 shows the TEM/BF microstructure images and SAED patterns acquired from the cross-sectioned CH couple. The presence of two areas filled with $Mg + Mg_2Ni$ eutectic mixtures was confirmed, i.e. close to the substrate (Fig. 9a) and farther away from it (Fig. 9c). In the first case, it is adjacent to the Mg₂Ni crystals, while for the latter - to pure magnesium.

4. Conclusions

For the first time, the high-temperature interaction of liquid magnesium with Ni substrate was studied experimentally using the sessile drop method and two different testing procedures: classical contact heating (CH) and non-contact heating of the Mg/Ni couple combined with capillary purification (CP) of the Mg drop from a native oxide film directly during wettability test.

Under the conditions of this study, in the case of the CP procedure, an oxide-free Mg drop showed the appearance of a wetting phenomenon on the Ni substrate in a sub-second time (an average contact angle $\theta < 90^{\circ}$ in < 1 s), followed by fast spreading and good wetting on the Ni substrate ($\theta_{(CP)} \sim 20^{\circ}$ in 5 s) to form a final contact angle of $\theta_{f(CP)} \sim 18^{\circ}$.

The SEM/EDS analysis of the cross-sectioned sessile drop couples revealed that the rapid spreading of liquid Mg over the Ni substrate is related to the reactive wetting, in which the dominant role is played by the dissolutive mechanism. It results in significant structural changes upon solidification of initially pure Mg that during the wettability test, was converted to Ni-saturated Mg alloy to form a complex solidified structure composed of Ni-rich MgNi₂ crystals surrounded with a small amount of the Mg₂Ni+Mg eutectic and reactively formed interfacial MgNi₂ layer.

Contrary to the Mg/Ni couple obtained by the CP procedure, the same couple of materials studied by the CH procedure showed dissimilar wetting and spreading behaviors, as well as the effects of substrate dissolution and mass transfer through the interface. The main reason for them is related to the presence of a thick oxide film on the Mg sample, preventing the formation of a symmetrical Mg drop and its spreading over the Ni substrate. Finally, it results in an apparently large contact angle mistakenly suggesting a non-wetting system. These findings confirm that the oxidation of the components and the presence of the native oxide film on the surface of contacting materials have a significant influence on the wetting behavior, spreading, and mutual dissolution of different materials at high temperatures.

The structural characterizations of the Mg/Ni couples showed that the reactive wetting between liquid Mg and Ni substrate is possible by two mechanisms: the dissolution of Ni in liquid Mg and the formation of new reaction products and the interfaces, however, the dissolutive wetting is the dominant one.

Moreover, the results of high-temperature interaction in the Mg/Ni couple obtained in this study by dissimilar CP and CH procedures show that pure Ni and Ni-rich alloys are not suitable as materials for direct long-term contact with liquid magnesium, e.g. as containers, crucibles, and other metallurgical appliances or parts of the devices used for high-temperature testing of molten Mg and its alloys. On the other hand, good wetting and fast spreading of liquid Mg in contact with solid Ni suggest Ni as a good candidate for use as a technological coating in joining Mg with dissimilar non-wettable materials, as well as in the synthesis of cast Mg-matrix composites.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

S. Terlicka: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing – original draft, Writing – review & editing. N. Sobczak: Conceptualization, Data curation, Formal analysis, Funding acquisition, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. L. Maj: Investigation, Writing – original draft. P. Darłak: Investigation. J.J. Sobczak: Funding acquisition, Methodology, Project administration, Isration, Resources, Supervision, Methodology, Project administration, Resources, Supervision, Methodology, Project administration, Resources, Supervision.

Acknowledgments

This research was supported by the National Science Centre of Poland within OPUS 16 Project, no. 2018/31/B/ST8/01172.

References

- [1] N. Sobczak, M. Singh, R. Asthana, Curr. Opin. Solid State Mater. Sci. 9 (4–5) (2005) 241–253, doi:10.1016/j.cossms.2006.07.007.
- [2] N. Eustathopoulos, N. Sobczak, A. Passerone, K. Nogi, J. Mater. Sci. 40 (2005) 2271–2280, doi:10.1007/s10853-005-1945-4.
- [3] N. Eustathopoulos, M.G. Nicholas, B. Drevet, Wettability At High Temperatures, first ed., Pergamon, 1999 Boston.
- [4] N. Sobczak, J. Sobczak, R. Asthana, R. Purgert, China Foundry 7 (4) (2010) 425–443.
- [5] A. Kudyba, N. Sobczak, W. Polakowski, G. Bruzda, A. Polkowska, D. Giuranno, J. Magnes. Alloy. 9 (15) (2021) 183–191, doi:10.1016/j. jma.2020.06.003.
- [6] N. Eustathopoulos, Metals 5 (1) (2015) 350–370, doi:10.3390/ met5010350.
- [7] A. Kudyba, N. Sobczak, P. Turalska, G. Bruzda, A. Makaya, L. Pambaguian, Trans. FRI 58 (1) (2018) 47–53, doi:10.7356/iod.2018.05.
- [8] J. Tan, S. Ramakrishna, Appl. Sci. 11 (15) (2021) 6861, doi:10.3390/ app11156861.
- [9] S. Terlicka, P. Darłak, N. Sobczak, J.J. Sobczak, Materials 15 (24) (2022) 9024, doi:10.3390/ma15249024.
- [10] W. Xu, H. Li, J. Yang, Y. Zhao, J.P. Oliveira, H. Liu, Z. Zhang, C. Tan, J. Manuf. Process. 80 (2022) 600–611, doi:10.1016/j.jmapro.2022.06. 042.
- [11] A.M. Nasiri, Y. Zhou, Sci. Technol. Weld. J., 20 (2015) 155–163, doi:10. 1179/1362171814Y.000000264.
- [12] R. Cao, J.H. Chang, Q. Huang, X.B. Zhang, Y.J. Yan, J.H. Chen, J. Manuf. Mater. Process. 31 (2018) 674–688, doi:10.1016/j.jmapro.2018. 01.001.
- [13] A.M. Nasiri, M.Y. Lee, D.C. Weckman, Y. Zhou, Metall. Mater. Trans. A 45 (2014) 5749–5766, doi:10.1007/s11661-014-2514-8.
- [14] J. Yang, Z. Yu, Y. Li, H. Zhang, N. Zhou, Sci. Technol. Weld. Join. 23
 (7) (2018) 543–550, doi:10.1080/13621718.2018.1425182.
- [15] K. Kondoh, M. Kawakami, H. Imai, J. Umeda, H. Fujii, Acta Mater. 58 (2) (2010) 606–614, doi:10.1016/j.actamat.2009.09.039.
- [16] S. Terlicka, N. Sobczak, J.J. Sobczak, P. Darłak, E. Ziółkowski, J Mater. Eng. Perform. 32 (2023) 5689–5696, doi:10.1007/s11665-023-07950-1.
- [17] N. Sobczak, A. Bellosi, T. Kosmač, A.P. Tomsia, in: Interfacial Science in Ceramic Joining, 58, Springer, 1998, pp. 27–42, doi:10.1007/ 978-94-017-1917-9_3. NATO ASI SeriesDordrecht.
- [18] E. Ziółkowski, J.J. Sobczak, P. Fima, N. Sobczak, in: Metalurgia, 2020, pp. 519–530. ISBN 978-83-63605-51-3 (in Polish).
- [19] Y.S. Touloukian, R.K. Kirby, R.E. Taylor, P.D. Desai, Y.S. Touloukian, C.Y. Ho, in: Thermophysical Properties of Matter, Plenum, 1977, pp. 194–200. New YorkISBN (Vol. 12) 0-306-67032-1.
- [20] Y.S. Touloukian, R.K. Kirby, R.E. Taylor, P.D. Desai, Y.S. Touloukian, C.Y. Ho, in: Thermophysical Properties of Matter, Plenum, 1977, pp. 288–301. New YorkISBN (Vol. 13) 0-306-67033-X.
- [21] N. Sobczak, A. Kudyba, R. Nowak, W. Radziwill, K. Pietrzak, Pure Appl. Chem. 79 (10) (2007) 1755–1769, doi:10.1351/pac200779101755.
- [22] A. Passerone, F. Valenza, M.L. Muolo, M. Ferrari, L. Liggieri, R. Miller, in: Drops and Bubbles in Contact With Solid surfaces. Progress in Colloid and Interface Science, CRC Press, 2013, pp. 299–334. ISBN: 978-1-4665-7545-5.
- [23] R. Asthana, N. Sobczak, M. Singh, Int. J. Appl. Ceram. Technol. 19 (2021) 1029–1049, doi:10.1111/ijac.13972.
- [24] S. Terlicka, N. Sobczak, Ł. Maj, P. Darłak, J.J. Sobczak, J. Mol. Liq. 387 (2023) 122730, doi:10.1016/j.molliq.2023.122730.
- [25] FactSage version 8.2 with FTlite database. Available online: https:// www.crct.polymtl.ca/fact (accessed on 01 June 2023).