DOI: 10.24425/amm.2019.126267

M. SULIGA*#, R. WARTACZ*, H. KANIA**

RESEARCH OF ZINC COATINGS IN THIN MEDIUM CARBON STEEL WIRES

An analysis of the effect of drawing speed on the formation of a zinc coating in the multi-stage fine steel wire drawing process has been carried out in the article. Pre-hardened 2.2 mm-diameter material was drawn into 1.00 mm-diameter wire in 6 draws on a multi-stage drawing machine. The drawing process was carried out at a drawing speed of 5, 10, 15, 20 and 20 m/s, respectively. Mechanical tests were tests were performed for the final wires to determine their yield strength, ultimate tensile strength, uniform and total elongation and reduction in area. The thickness of the zinc coating on the wire surface was determined by the gravimetric method and based on metallographic examination. The use of electron scanning microscopy, on the other hand, enabled the identification of individual phases in the zinc coating. The above investigations were supplemented with corrosion testing of 1.00 mm-diameter wires. It has been demonstrated that drawing speed significantly influences not only the thickness of the zinc coating on the drawn wire surface, buts also its morphology and corrosion resistance.

Keywords: wire, zinc coating, drawing speed, mechanical properties

1. Introduction

Zinc-coated medium-carbon steel wires have a wide application in industry. Products manufactured from C42D steel wire include ropes and springs [1-2]. In their operation, these products must exhibit high tensile strength, standard values of reduction in area and uniform/total elongation [3-4], which is why the drawing speed, drawing die type, lubrication conditions and single/ total reduction magnitude are crucial for the finished product in the wire production process [5-7]. In the steel wire production process, multi-stage drawing machines are widely used, which enable wires to be drawn at speeds exceeding 20 m/s. Studies [1,7] show that in drawing at high speeds exceeding 20 m/s, intensive heating of the top wire layer occurs, which has a negative effect on the lubrication conditions and wire properties. In work [1] it has been shown that with increasing of drawing speed the heated surface layer thickness measured at the exit of the wire from the dies is reduced significantly. The decrease in the thickness of this layer can be explained by a shorter time of heat transfer to the wire, which causes additional heat accumulation in the surface layer.

When drawing zinc-coated wire, as a result of an effect of high temperatures on the wire and drawing die surfaces [8], an added problem in the drawing process is to obtain the zinc coating with properties conforming to applicable industry standards.

The drawing technology also affects the state of the surface layer of the wire, and thus the zinc coating. Corrosion resistance in a chloride-containing environment depends on the thickness of the zinc coating. The corrosion process of steel materials such as wires is interpreted as unintentional physicochemical destruction of material resulting from the environmental impact [9-13]. The degradation of the material, which is spread over time, is one of the main problems of using steel products.

The literature does not describe the effect of drawing speed on the properties of zinc-coated medium-carbon wires. The present study examines the effect of drawing speed on the wire properties and the formation of the zinc coating in the process of multi-stage drawing of fine steel wire.

2. Drawing material and technology

For the drawing process, 5.5 mm-diameter C42D grade medium-steel wire rod was used, which had been previously subjected to hot galvanizing process. The galvanizing process was conducted on a commercial continuous wire galvanizing and patenting line. After chemical surface preparation including degreasing, etching and fluxing, the wire rod drawn though a zinc bath. After exiting the zinc bath, the wire rod was air cooled.

The starting material was made in two stages. The first stage included drawing 5.5 mm-diameter wire rod into 2.2 mm-diameter wire in 7 draws on a Mario Frigerio multi-stage drawing machine, type S600/7, and then the pre-hardened

^{*} CZESTOCHOWA UNIVERSITY OF TECHNOLOGY, INSTITUTE OF PLASTIC FORMING AND SAFETY ENGINEERING , 42-200 CZĘSTOCHOWA, 19 ARMII KRAJOWEJ STR., POLAND

^{**} SILESIAN UNIVERSITY OF TECHNOLOGY, INSTITUTE OF MATERIAL SCIENCE, 8 KRASIŃSKIEGO STR., 40-019 KATOWICE, POLAND

[#] Corresponding author: suliga@wip.pcz.pl

2.2 mm-diameter wire was drawn in 6 draws on a S300/7-type Mario Frigerio drawing machine into 1.00 mm-diameter finished wire, as shown in Table 1. The drawing speed was 5, 10, 15, 20 and 20 m/s, respectively.

TABLE 1

The distribution of single reductions, G_p ; total reduction, G_c

Draft number	0	1	2	3	4	5	6	7
<i>ø</i> , mm	2.20	1.90	1.66	1.48	1.33	1.20	1.09	1.00
$G_p, \%$	—	25.41	23.67	20.51	19.24	18.59	17.49	15.83
$G_c, \%$	—	25.41	43.07	54.74	63.45	70.25	75.45	79.34

3. Mechanical properties and lubrication conditions

Mechanical tests on 1.00 mm-diameter zinc-coated wires were carried out on a Zwick/Z100 testing machine in the Laboratory of the Czestochowa University of Technology. For finished wires, mechanical tests were carried out to determine their yield strength (YS), ultimate tensile strength (UTS), uniform (EU) and total elongation (ET) and reduction in area (RA). Table 2 provides the results of the mechanical tests and the measurement of the lubricant quantity M on the wire surface.

Drawing speed v, m/s	YS, MPa	UTS, MPa	ЕТ, %	EU, %	RA, %	M, g/m ²
5	1518	1955	1.84	1.21	45.8	1.72
10	1546	2022	1.78	0.99	44.2	1.33
15	1602	2049	1.69	0.83	42.9	1.14
2.0	1624	2063	1.65	0.77	40.0	1.09

Mechanical test results and amount of lubricant on the wires surface

It can be noticed from the results shown in Table 2 that drawing speed markedly influences the mechanical properties of medium-steel wire. Wires drawn at a velocity of 20 m/s exhibited a yield strength value higher by 5.6% and an ultimate tensile strength value higher by 5.4%, compared to the material drawn at a velocity of 5 m/s. The higher mechanical values of the wires drawn at the drawing speed of 20 m/s can be deduced in the greater hardening of their surface layer. This is caused by a decrease in lubricant quantity (Table 2), which leads to an impairment of lubrication conditions in the multi-stage steel wire drawing process.

The presented test results confirm the adverse effect of drawing speed on the plastic properties of zinc-coated wire. The increase in drawing speed reduces the values of uniform elongation, total elongation and reduction in area. For the drawing speed of 20 m/s, a 12% decrease in uniform elongation was noted, compared to the drawing speed of 5 m/s. A similar declining trend, i.e. by nearly 40% of total elongation and 12% of reduction in area, is also observed for the aforementioned drawing speeds.

4. Examination of the zinc coating

Zinc coatings applied to wires shall meet the requirements of standard PN-EN 10244-2. According to this standard zinc coatings applied on wire should be smooth and uniformly distributed, with no defects in the form of dross contaminants and uncoated spots.

Test samples were taken from either end of the coil, and only those were selected, which were free from surface damage. The test variant covered 10 wires, each 10 cm long, which were subjected to coating mass determination in accordance with standard EN 10244-1. The specimens were cleaned and degreased, and then weighed prior to the removal of the zinc coating. For removing the zinc coating, hydrochloric acid was used, to which an inhibitor in the form of hexamethylenetetramine (urotropin) was added. Antimony chloride (3.2 g) was dissolved in concentrated hydrochloric acid (500 ml), and then the obtained solution was diluted with distilled water (to 1000 ml). The test specimens were immersed in the solution until the zinc coating was removed. After removing the coating, the wires were cleaned and degreased and then weighed again. The results are shown in Table 3 and in Figure 1.

TABLE 3

The results of the zinc coating measurements (average values) for wires drawn at a speed of 5, 10, 15, 20 m/s, respectively, where: δ – mass of zinc on the wire surface, g/m²; g – zinc coating thickness, µm

<i>v</i> , m/s	δ , g/m ²	<i>g</i> , μm	The class of wire according to PN-EN 10244-2 standard
5	101.20	14.19	В
10	95.06	13.33	В
15	88.72	12.44	В
20	52.18	7.31	D



Fig. 1. The effect of drawing speed on the mass of zinc on the surface of 1.0 mm-diameter wires

It can be concluded from the data illustrated in Figure 1 that drawing speed significantly influences the mass of the zinc coating on wires after the drawing process. Wires drawn at a drawing speed of 5 m/s had a zinc coating mass almost two times that of

TABLE 2

wires drawn at a drawing speed of 20 m/s. The PN-EN 10244-2 standard, which is commonly used in the steelmaking industry, specifies the minimum thickness of coatings by categorizing them into respective classes. As zinc-coated 1.00 mm-diameter wires after drawing are categorized into Class B, $\delta \ge 80$ g/m², it can be noticed that wires drawn within the drawing speed range of 5-15 m/s meet the condition for remaining in Class B. By contrast, the coating that has remained on wires drawn at the drawing speed of 20 m/s can be, based on its thickness, assigned exclusively to the lowest Class D $60 > \delta > 25$ g/m². Zinc coatings of such a small thickness do not guarantee the sufficient corrosion resistance of wire and wire products.

The quality of a zinc coating is defined not only by the mass of zinc on the wire surface, but also by the analysis of the phase equilibrium of the Fe-Zn alloys of individual structural constituents and the determination of the place of their occurrence in the zinc coating. The examination of the microstructure and chemical composition of coatings was made using an S-3400 N-type Hitachi scanning microscope equipped with an Energy Dispersion Spectroscopy X-ray spectrometer. An accelerating voltage of 25 kV was used. The quantitative chemical analysis was conducted on the cross-sections of selected zinc-coated specimens regarded as representative, using the System Six

software by Noram Instruments. The microstructure of coatings obtained after drawing at varying speeds is shown in Fig. 2.

The coatings obtained on the finished 1 mm-diameter wire after the drawing process were distinguished by a bright and shiny appearance. Such an appearance shows the presence of a continuous outer layer. After drawing, the coating has a typical two-layered structure. At the substrate, a diffusion layer of the Fe-Zn system phases is visible, which is covered by the outer zinc layer. However, no clear boundaries between individual Fe-Zn intermetallic phase layers can be distinguished within the diffusion layer. Such a diffusion layer structure is not typical of zinc coatings. In a zinc coating immediately after its fabrication, layers of the intermetallic phases Γ , δ_1 i ζ with clearly distinguished boundaries form within the diffusion layer [14]. Moreover, the ζ phase traditionally forms a boundary with the outer coating layer (η) in the form of densely packed crystals perpendicular to the coated surface [15]. By contrast, at the boundary with the substrate, zinc coatings generally show a high uniformity of the interface [16-17]. The wire coatings obtained after drawing, besides the absence of defined phases in the diffusion layer, have a very uneven interface with the substrate. In addition, it can be noticed that the coating/substrate interface (Fig. 2) becomes more uneven with the increase in drawing speed.



Fig. 2. The (SEM) coating microstructure on the cross-section of C42D medium-carbon steel wire after having been drawn into a diameter of 1 mm at a drawing speed of: a) 5 m/s, b) 10 m/s, c) 15 m/s, d) 20 m/s

416

Microanalysis made to determine the chemical composition in the micro-regions of the coating allows one to identify phases occurring in the coating. In coatings obtained after drawing at the speed of 5 m/s (Fig. 3a) and 20 m/s (Fig. 3b), the occurrence of zinc can be found in points 1 and 4, respectively, with a slight amount of iron dissolved in it. The chemical composition of this layer may correspond to the η phase, forming an outer layer of the coating. In the diffusion layer, 8.0 wt% (pt 2) and 7.6 wt% (pt 5) Fe were found in its upper zone, while 12.7 wt% (pt 3) and 13.1 wt% (pt 6) Fe in its lower zone. Such an iron content of the Fe-Zn phase corresponds to the range of stability of the δ_1 phase. No other structural constituents were observed in the morphology of the diffusion layer on the wire cross-section. This may suggest that the diffusion layer of a coating after plastic working has no ζ phase layer, which is present as standard in zinc coatings that are not subjected to plastic working [14-15].



Fig. 3. The (SEM) diffusion layer microstructure and the EDS X-ray spectral analysis in micro-regions of the coating on the cross-section of C42D medium-steel wire after drawing into the diameter of 1 mm at a drawing speed of a) 5 m/s, and b) 20 m/s

TABLE 4

Chemical composition in selected micro-regions of the coating obtained on C42D medium-steel wire after drawing into the diameter

	Chemical composition						
Point of analysis	Fe	-K	Zn-K				
anarysis	%mas.	%at.	%mas.	%at.			
pt 1	1.7	1.9	98.3	98.1			
pt 2	8.0	9.3	92.0	90.7			
pt 3	12.7	14.6	87.3	85.4			
pt 4	1.4	1.6	98.6	98.4			
pt 5	7.6	8.8	92.4	91.2			
pt 6	13.1	15.0	86.9	85.0			
pt 7	-	-	100.0	100.0			
pt 8	6.5	7.6	93.5	92.4			
pt 9	8.4	9.7	91.6	90.3			

of 1 mm (points of analysis as per Figs. 3 and 4)

Figure 4 shows the structure of the coating on the longitudinal section of wire drawn at the drawing speed of 20 m/s. In this section, along the wire axis, the interface between the coating and the substrate exhibits high uniformity. Such a morphology at the steel substrate-zinc coating interface should be regarded as typical [17].

Therefore, the observed high non-uniformity of this interface at the wire cross-section (Fig. 3) may most likely be caused by the drawing process carried out and drawing die pressure on the hard phases of the Fe-Zn system. The X-ray microanalysis shows the occurrence of zinc in the outer coating layer (pt 7, Fig. 4b, Table 4). The diffusion layer, on the other hand, contains 8.4 wt% Fe (pt 9), which may correspond to the content of iron in the δ_1 phase. In the upper zone of the diffusion layer, there exist regions of a lower iron content -6.5 wt% (pt 8). This chemical composition corresponds to the range of stability of the ζ phase. However, it is hard to distinguish the boundaries of this phase and to definitely confirm its presence in the coating structure. It should be noted that the drawing process heats the wire surface up to a temperature exceeding 500°C. In such conditions, restructuring may take place both within the diffusion layer, as well as in the outer layer, leading to the formation of phases with higher iron contents. At a similar temperature during annealing of zinc coatings on sheet (so-called galvannealing coatings), a resumption of reaction diffusion processes occurs, which leads to the formation of a coating built chiefly of the phase δ_1 , with only a small fraction of the ζ phase [19]. Moreover, according to the Fe-Zn equilibrium system, the ζ phase is not stable above the temperature of 520°C [20]. The heating up of wire during drawing can therefore be explained by either the absence or presence only a small quantity of the ζ phase, which has most likely been transformed at high temperature into the δ_1 phase. The presence of a larger fraction of the δ_1 phase might be advantageous because of its corrosion resistance. Zinc coatings fabricated in the high-temperature galvanizing process, whose structure shows no presence of the ζ phase and a greater fraction of the δ_1 phase, exhibit corrosion resistance about 2 times better than that of the traditional zinc coatings [21].

In the diffusion layer of the coating, the occurrence of cracks can also be observed, both in the transverse direction and in the longitudinal direction. In zinc coatings, the δ_1 phase shows a tendency to spontaneous cracking in the transverse direction across the whole layer thickness [18]. In the observed



Fig. 4. The (SEM) diffusion layer microstructure and the EDS X-ray spectral analysis in micro-regions of the coating on the longitudinal section of C42D medium-steel wire after drawing into the diameter of 1 mm at the drawing speed of 20 m/s

418

cross-section of the coating on the drawn wire, the transverse cracks do not propagate through the whole layer thickness and have a distorted shape, which might suggest that they formed during the drawing process. In addition, longitudinal cracks are observed in the outer layer, which do to occur spontaneously in zinc coatings. The presence of cracks in the diffusion layer does not lead, however, to the loss of its integrity and delaminations from the substrate. It is favourable that the structure of an obtained coating has an outer zinc layer exhibiting good plastic properties, which will protect the coating against delamination during a possible future plastic working operation.

5. Corrosion testing in artificial atmospheres

The corrosion resistance of the coatings was determined comparatively in the standard corrosion test in neutral salt mist. Based on the PN-EN ISO 9227 standard, corrosion testing was performed on fine zinc-coated wires in artificial atmospheres. This test is particularly useful for detecting discontinuous, such as pores and other surface defects.

For testing, an Erichsen CORROTHERM Model 610 salt spray chamber was used, which had a working volume of over 0.4 m³, because smaller chambers might give rise to a problem with spraying the salt solution in a uniform manner. It is necessary to make sure that the salt spray chamber meets the conditions for the uniformity of salt spray distribution. The upper part of the chamber should be designed in a manner that prevents the sprayed solution from dripping onto the test specimens, see Figure 5. Testing in a mist of 5% sodium chloride water solution at a temperature of 35°C should be conducted at a pressure controlled in the range from 70 to 170kPa. The concentration of the spayed salt solution should range from 6.5 do7.2 pH.

Wires of a diameter of 1 mm were wound onto a 22 mmdiameter tube to form a spring consisting of 35 coils. Zinc-coated wire springs were fixed in such a manner that each of the coils was inclined to the perpendicular at an angle of 20°. The test specimens were arranged on different levels in the chamber so that they did not contact with one another and were not directly in the way of the solution sprayed by the atomizer. The specimen testing duration was divided into cycles of 8 hours' chamber operation for 6 days. The test specimens were assessed for appearance every 24 hours. To determine unit mass changes during the test, gravimetric examinations were made after 48 and 96 hours of specimen exposure in the salt spray chamber. The results are illustrated in Figure 6 and 7.

The appearance of the surface of wires drawn at a drawing speed of 5 and 20 m/s, respectively, during corrosion testing is shown in Fig. 6. Prior to starting corrosion testing (Fig. 6a), the coating surface had a bright and shiny appearance. No coating discontinuities were found on the surface of the test specimens. At the initial stage of the corrosion process, already after 24 hours of salt spray exposure, the total coverage of the coating surface with white corrosion products was noticed, which indicates a progressing corrosion of the zinc coating. After 48 hours of exposure (Fig. 6b), on the other hand, first red corrosion products were found to have occurred on the test specimen surface. While on the specimen of wire drawn at the speed of 5 m/s this was a rust-coloured discolouration that might indicate a progressing corrosion of the intermetallic Fe-Zn phases of the diffusion layer of the coating, the wire drawn at the speed of 20 m/s clearly showed punctures in the coating reaching the substrate and a progressing corrosion of the steel substrate (indicated with the arrow in Fig. 6b). After 96 hours of salt spray testing (Fig. 6c), a large part of the specimen surface was covered with red corrosion products, indicating the lost of the protective ability of the zinc coating. It can be noticed, however, that slightly more white corrosion products have remained on the specimen of wire drawn at the speed of 5 m/s, which suggests that the corrosion progressed in this case at a lower rate.

From the coating mass change during salt spray exposure it can be found the coatings tested have shown a mass increase. The measurement of specimen mass change taken after 48 hours of corrosion testing (Fig. 8) found that the greatest percentage mass increment was exhibited by the coating drawn at the speed of 20 m/s. It could also be found that the mass of corrosion



Fig. 5. The CORROTHERM Model 610 salt spray chamber



Fig. 6. The appearance of wire surface during corrosion testing in the salt spray chamber



Fig. 7. The appearance of wire drawn with speed 20 m/s after 96 hours in the salt spray chamber





Fig. 8. Percentage mass change of specimens of zinc-coated wire drawn at different speeds during salt spray testing after 48 hours of exposure and after the completion of the corrosion test and removal of the corrosion products

products forming on the surface increased with increasing wire drawing speed. After the completion of the corrosion test (after 96 hours) and removal of the corrosion products from the wire surface (Fig. 8), the largest percentage mass loss was shown also by wires drawn at the speed of 20 m/s. It can therefore be concluded that the speed of drawing zinc-coated wire affects the corrosion resistance, which decreases with increasing drawing speed.

5. Conclusions

- 1. After the process of drawing wire at a drawing speed of 5-20 m/s, zinc coatings produced on the wire do not show any discontinuities and have a two-layered structure. The diffusion layer present at the interface with the substrate is responsible for the adhesion of the coating, while the outer zinc layer provides a plastic protection of the brittle intermetallic Fe-Zn phases during the subsequent plastic working of the wire.
- Zinc coatings after having been drawn at a drawing speed of 5-20 m/s are built chiefly of the phase d₁ that forms the diffusion layer of the coating, and an outer layer of the solution of iron in zinc, η. Either a disappearance or the existence of only a small quantity of the ζ, phase is observed in the coating, which is most likely caused by the transformation of this phase into the phase δ₁ as the wire is heated up to a high temperature during the drawing process.
- 3. The speed of drawing zinc-coated wire affects the corrosion resistance of the wire. Increasing the drawing speed will result in a reduction of the corrosion resistance of the wire.

REFERENCE

- [1] M. Suliga, Analiza wielostopniowego ciągnienia drutów stalowych z dużymi prędkościami w ciągadłach konwencjonalnych i hydrodynamicznych, Seria Monografie nr 32, Wyd. Wydz. Inżynierii Procesowej, Materiałowej i Fizyki Stosowanej Politechniki Częstochowskiej, Częstochowa (2013).
- [2] B. Goli, F. Knap, J. Pilarczyk, Wybrane zagadnienia z teorii i praktyki ciagnienia, Skrypty Politechniki Częstochowskiej, część 6, Wydawnictwo Politechniki Częstochowskiej, Czętochowa (1997).
- [3] J.G. Wistreich, The Fundamentals of wire drawing. Metallurgical Reviews 3, 10, 97-141 (1958).
- [4] M. Suliga, Analysis of the heating of steel wires during high speed multipass drawing process. Archives of Metallurgy and Materials 59, 4, 1475-1480 (2014).
- [5] F. Knap, R. Karuzel, Ł. Cieślak, Ciągnienie drutów, prętów i rur, Metalurgia Nr 36, Wyd. Wydz. Inżynierii Procesowej, Materiałowej i Fizyki Stosowanej Politechniki Częstochowskiej, Częstochowa (2004).

- [6] F. Knap, L. Latacz-Pilarczyk, J. Pilarczyk, Badanie wpływu kąta stożka zgniatającego ciągadła na własności mechaniczne drutu do konstrukcji sprężonych, Zeszyty Naukowe Politechniki Częstochowskiej 89, 9, 21-34 (1974).
- [7] J. Łuksza, Elementy ciągarstwa, AGH, Kraków (2001).
- [8] J. Łuksza, J. Majta, Odkształcenia zbędne w prętach i drutach ciagnionych, Hutnik 4, 134-137 (1989).
- [9] H. Bala, Korozja, Wydawnictwo Politechniki Częstochowskiej, Częstochowa (2003).
- [10] J. Baszkiewicz, M. Kamiński, Podstawy korozji materiałów, Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa (2006).
- [11] L.A. Dobrzański, Podstawy nauki o materiałach i metaloznawstwo, WNT, Warszawa-Gliwice (2002).
- [12] Z. Panossian, L. Mariaca, M. Morcillo, S. Flores, J. Rocha, J.J. Peña, et al., Steel cathodic protection afforded by zinc, aluminium and zinc/aluminium alloy coatings in the atmosphere, Surf. Coatings Technol. **190**, 244-248 (2005).
- [13] E. Almeida, M. Morcillo, B. Rosales, Atmospheric corrosion of zinc, Part 2, Marine atmospheres, British Corrosion Journal 35, 4, 289-296 (2000).
- [14] H. Kania, P. Liberski, Synergistic Influence of the Addition of Al, Ni and Pb to a Zinc Bath upon Growth Kinetics and Structure of Coatings. Solid State Phenomena 212, 115-120 (2014).
- [15] P. Pokorny, J. Kolisko, L. Balik, P. Novak, Description of structure of Fe-Zn intermetalic compounds present in hot-dip galvanized coatings on steel, Metalurgija 54, 4, 707-710 (2015).
- [16] H. Kania, P. Liberski, Synergistic influence of Al, Ni, Bi and Sn addition to a zinc bath upon growth kinetics and the structure of coatings. IOP Conf. Series: Materials Science and Engineering 35, 01, 2012 (2004).
- [17] W.D. Schulz, M. Thiele, Feueverzinken von Stückgut, Eugen G. Leuze Verlag (2008).
- [18] S. Ploypech, Y. Boonyongmaneerat, P. Jearanaisilawong, Influence of thickness of intermetallic layers on fracture resistance of galvanized coatings, Surface and Coatings Technology 206, 3758-3763 (2012).
- J.M. Long, D.A. Haynes, P.D. Hodgson, Characterisation of galvanneal coatings on strip steel, Materials forum 27, 62-67 (2004).
- [20] O. Kubaschewski, Iron binary phase diagrams. Springre-Verlag, Berlin (1982).
- [21] P. Liberski, at al., Corrosion resistance of zinc coatings obtained in high-temperature baths, Materials Science 39, 652-657 (2003).